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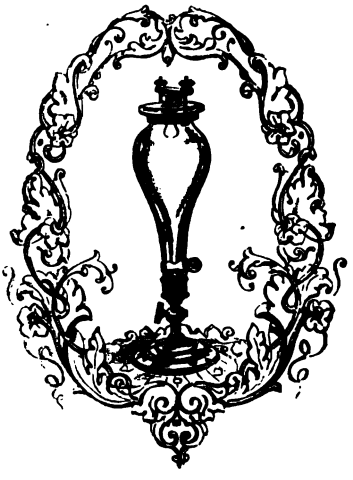

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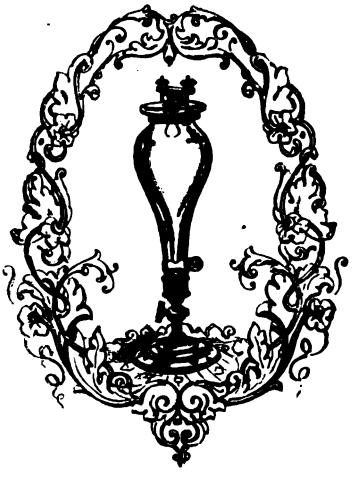

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CONTENTS OF VOL. V.

METALS (*continued*).

Page

CHAPTER XXVIII. ZINC.

Memoirs, &c. relating to Zinc 1
History.—Sources.—Preparation 1
Purification 2
Properties 4

COMPOUNDS OF ZINC.

Zinc and Oxygen.

Suboxide of Zinc? 4
Zinc-oxide.—ZnO. 5
Hydrate of Zinc-oxide 11
Zinc-salts. 12
Peroxide of Zinc. 13

Zinc and Hydrogen.

Hydride of Zinc. 13
Zincuretted Hydrogen gas? 13

Zinc and Carbon.

Carbide of Zinc? 13
Carbonate of Zinc-oxide 13
a. Octobasic.—*b*. Quadrobasic. 14
c. With 2 At. acid to 5 At. base 14
d. Bibasic.—*e*. Monobasic 15
¶ *Manganiferous Zinc-spar* 16
¶ *Ferruginous Zinc-spar; Kapnite?* 16
f. Acid salt ....

Zinc and Boron.

Borate of Zinc-oxide 17

Zinc and Phosphorus.

Phosphide of Zinc 17
Hypophosphite of Zinc-oxide 17
Phosphite of Zinc-oxide 17

Page

Ordinary Phosphate of Zinc-oxide.
a. Triphosphate 17
b. Diphosphate.—*c.* Acid Phosphate 18
Pyrophosphate of Zinc-oxide 18
Metaphosphate of Zinc-oxide 18

Zinc and Sulphur.

Sulphide of Zinc 19
Hydrated Sulphide 20
Oxysulphide of Zinc 20
Hyposulphite of Zinc-oxide 21
Tetrathionate of Zinc-oxide 21
Trithionate of Zinc-oxide 21
Sulphite of Zinc-oxide.... 21
Hyposulphate of Zinc-oxide 22
Sulphate of Zinc-oxide.
a. Octobasic.—*b.* Sexbasic.—*c.* Quadrobasic 22
d. Bibasic 23
e. Monobasic 23
α. Mono-hydrated 24
β. Bi-hydrated.—*γ.* With 3½ At. water.—*δ.* Penta-hydrated 25
ε. Sex-hydrated.—*ζ.* Hepta-Hydrated. 26
f. Bisulphate 26
Sulphocarbonate of Zinc 26
Sulphide of Phosphorus and Zinc 26

Zinc and Selenium.

Selenide of Zinc 27
Hydrated Selenide 27
Selenite of Zinc-oxide.
a. Monoselenite.—*b.* Biselenite.—¶ *c.* Quadroselenite 27
Seleniate of Zinc-oxide 28

Zinc and Iodine.

Iodide of Zinc 28
Hydriodate of Zinc-oxide 28
Oxy-iodide of Zinc 28
Hydriodite of Zinc-oxide 29
Iodide of Zinc-oxide ? 29
Iodate of Zinc-oxide 29

Zinc and Bromine.

Bromide of Zinc 29
Hydrobromate of Zinc-oxide.... 29
Bromate of Zinc-oxide 30

Zinc and Chlorine.

Chloride of Zinc 30
Hydrochlorate of Zinc-oxide 31

CONTENTS OF VOL. V.

METALS (*continued*).

Page

CHAPTER XXVIII. ZINC.

Memoirs, &c. relating to Zinc 1
History.—Sources.—Preparation 1
Purification 2
Properties 4

COMPOUNDS OF ZINC.

Zinc and Oxygen.

Suboxide of Zinc? 4
Zinc-oxide.—ZnO. 5
Hydrate of Zinc-oxide 11
Zinc-salts. 12
Peroxide of Zinc. 13

Zinc and Hydrogen.

Hydride of Zinc. 13
Zincuretted Hydrogen gas? 13

Zinc and Carbon.

Carbide of Zinc? 13
Carbonate of Zinc-oxide 13
a. Octobasic.—*b.* Quadrobasic 14
c. With 2 At. acid to 5 At. base 14
d. Bibasic.—*e.* Monobasic 15
¶ *Manganiferous Zinc-spar* 16
¶ *Ferruginous Zinc-spar; Kapnite?* 16
f. Acid salt ....

Zinc and Boron.

Borate of Zinc-oxide 17

Zinc and Phosphorus.

Phosphide of Zinc 17
Hypophosphite of Zinc-oxide 17
Phosphite of Zinc-oxide 17

Page

Ordinary Phosphate of Zinc-oxide.
a. Triphosphate 17
b. Diphosphate.—*c.* Acid Phosphate 18
Pyrophosphate of Zinc-oxide 18
Metaphosphate of Zinc-oxide 18

Zinc and Sulphur.

Sulphide of Zinc 19
Hydrated Sulphide 20
Oxysulphide of Zinc 20
Hyposulphite of Zinc-oxide 21
Tetrathionate of Zinc-oxide 21
Trithionate of Zinc-oxide 21
Sulphite of Zinc-oxide.... 21
Hyposulphate of Zinc-oxide 22
Sulphate of Zinc-oxide.
a. Octobasic.—*b.* Sexbasic.—*c.* Quadrobasic 22
d. Bibasic 23
e. Monobasic 23
α. Mono-hydrated 24
β. Bi-hydrated.—*γ.* With 3½ At. water.—*δ.* Penta-hydrated 25
ε. Sex-hydrated.—*ζ.* Hepta-Hydrated. 26
f. Bisulphate 26
Sulphocarbonate of Zinc 26
Sulphide of Phosphorus and Zinc 26

Zinc and Selenium.

Selenide of Zinc 27
Hydrated Selenide 27
Selenite of Zinc-oxide.
a. Monoselenite.—*b.* Biselenite.—¶ *c.* Quadroselenite 27
Seleniate of Zinc-oxide 28

Zinc and Iodine.

Iodide of Zinc 28
Hydriodate of Zinc-oxide 28
Oxy-iodide of Zinc 28
Hydriodite of Zinc-oxide 29
Iodide of Zinc-oxide? 29
Iodate of Zinc-oxide 29

Zinc and Bromine.

Bromide of Zinc 29
Hydrobromate of Zinc-oxide.... 29
Bromate of Zinc-oxide 30

Zinc and Chlorine.

Chloride of Zinc 30
Hydrochlorate of Zinc-oxide 31

Page
Oxychloride of Zinc 31
Hypochlorite of Zinc-oxide.... 32
Chlorate of Zinc-oxide 32
Perchlorate of Zinc-oxide 33

Zinc and Fluorine.

Fluoride of Zinc 33
Hydrofluate of Zinc-oxide 33
Fluoboride of Zinc 33

Zinc and Nitrogen.

Nitride of Zinc 33
Nitrate of Zinc-oxide.
a. Octobasic.—*b.* Quadrobasic.—*c.* Monobasic 34
Zinc-oxide with Ammonia (*Zincate of Ammonia*) 35
Carbonate of Zinc-oxide and Ammonia 36
Boride of Nitrogen and Zinc? 36
Ordinary Phosphate of Zinc-oxide and Ammonia 36
Pyrophosphate of Zinc-oxide and Ammonia 37
Metaphosphate of Zinc-oxide and Ammonia 37
Ammonio-hyposulphite of Zinc-oxide 37
Ammonio-hyposulphate of Zinc-oxide 37
Quadrobasic Zinc-sulphate with Ammonia 37
Monobasic Zinc-sulphate with Ammonia.
a. $5NH^3 + 2(ZnO,SO^3)$.—*b.* $2NH^3 + ZnO,SO^3$ 38
c. $NH^3 + ZnO\ SO^3$ 39
Sulphate of Zinc-oxide and Ammonia 39
Ammonio-iodide of Zinc 40
Iodide of Zinc and Ammonium 40
Ammonio-iodate of Zinc-oxide 40
Ammonio-bromide of Zinc 40
Ammonio-bromate of Zinc-oxide 40
Ammonio-chloride of Zinc.
a. $2NH^3,ZnCl$.—*b.* $NH^3,ZnCl$.—*c.* $NH^3,2ZnCl$ 41
Chloride of Zinc and Ammonium 42

Zinc and Potassium.

Alloy of Zinc and Potassium 42
Zinc-oxide with Potash (*Zincate of Potash*) 43
Carbonate of Zinc-oxide and Potash 43
Sulphate of Zinc-oxide and Potash 43
Iodide of Zinc and Potassium 44
Chloride of Zinc and Potassium 44
Fluoride of Zinc and Potassium 44

Zinc and Sodium.

Alloy of Zinc and Sodium 44
Zinc-oxide with Soda (*Zincate of Soda*) 44
Carbonate of Zinc-oxide and Soda 45
Zinc-oxide with Fluxes 45
Sulphate of Zinc-oxide and Soda 45

Page

Iodide of Zinc and Sodium 45
Chloride of Zinc and Sodium 45

Zinc and Barium.

Iodide of Zinc and Barium 45

Zinc and Magnesium.

Sulphate of Zinc-oxide and Magnesia 46

Zinc and Aluminum.

Aluminate of Zinc-oxide 46
Sulphate of Alumina and Zinc-oxide: *Zinc-alum* 46
Fluoride of Aluminum and Zinc 46

Zinc and Silicium.

Silicate of Zinc-oxide: *Zinc-glance* 46
Hydrofluate of Silica and Zinc-oxide 47
Silicate of Zinc-oxide and Potash 47

Zinc and Tungsten.

Tungstate of Zinc-oxide 47
Sulphotungstate of Zinc: ZnS,WS^3 47

Zinc and Molybdenum.

Molybdate of Zinc-oxide 47
Sulphomolybdate of Zinc 47
Persulphomolybdate of Zinc 47
Molybdate of Zinc-oxide and Ammonia, and Molybdate of Zinc-oxide and Potash 48

Zinc and Vanadium.

Vanadiate of Zinc-oxide.
a. Monovanadiate.—*b*. Bivanadiate 48

Zinc and Chromium.

Chromate of Zinc-oxide.
a. Dichromate.—*b*. Monochromate 48
Chromate of Zinc-oxide and Potash 48

Zinc and Uranium.

Uranate of Zinc-oxide 49

Zinc and Manganese.

Permanganate of Zinc-oxide 49

Zinc and Arsenic.

Arsenide of Zinc 49
Arseniate of Zinc-oxide.
a. Tris-arseniate.—*b*. Acid salt 49
Hyposulpharsenite of Zinc 49
Sulpharsenite of Zinc.... 49
Sulpharseniate of Zinc 50
Arseniate of Zinc-oxide with Ammonia 50

Page

Zinc and Antimony.

Antimonide of Zinc 50
Antimoniate of Zinc-oxide 50
Sulphantimoniate of Zinc.—$3ZnS,SbS^5$ 50

Zinc and Tellurium.

Telluride of Zinc 51
Tellurite of Zinc-oxide 51
Sulphotellurite of Zinc.—$3ZnS,TeS^3$ 51

Zinc and Bismuth.

Alloy of Zinc and Bismuth ? 51
Other Compounds of Zinc 51

CHAPTER XXIX. CADMIUM.

Memoirs, &c.—History.—Sources.—Preparation 52
Properties 53

COMPOUNDS OF CADMIUM.

Cadmium and Oxygen.

Suboxide of Cadmium ? 53
Cadmic Oxide,—CdO 54
Hydrate of Cadmic Oxide 54
Cadmic Salts 55

Cadmium and Carbon.

Carbonate of Cadmic Oxide 55

Cadmium and Boron.

Borate of Cadmic Oxide 56

Cadmium and Phosphorus.

Phosphide of Cadmium 56
Hypophosphite of Cadmic Oxide 56
Phosphite of Cadmic Oxide 56
Ordinary Phosphate of Cadmic Oxide 56
¶ Pyrophosphate of Cadmic Oxide 56
Metaphosphate of Cadmic Oxide 57

Cadmium and Sulphur.

Sulphide of Cadmium (*Greenockite*) 57
Sulphite of Cadmic Oxide 58
Hyposulphate of Cadmic Oxide.... 58
Sulphate of Cadmic Oxide.
a. Disulphate.—*b.* Monosulphate 58
Sulphocarbonate of Cadmium 58

Cadmium and Selenium.

¶ Selenite of Cadmic Oxide 59

Page

Cadmium and Iodine.

Iodide of Cadmium 59
Iodate of Cadmic Oxide 59

Cadmium and Bromine.

Bromide of Cadmium 59
Hydrobromate of Cadmic Oxide 60
Bromate of Cadmic Oxide 60

Cadmium and Chlorine.

Chloride of Cadmium.
Hydrochlorate of Cadmic Oxide 60
Perchlorate of Cadmic Oxide 60

Cadmium and Fluorine.

Fluoride of Cadmium.... 61

Cadmium and Nitrogen.

Nitride of Cadmium ? 61
Nitrate of Cadmic Oxide 61
Ammoniacal Oxide of Cadmium 61
Ammonio-hyposulphate of Cadmic Oxide 61
Ammonio-sulphate of Cadmic Oxide 62
Ammonio-iodide of Cadmium 62
Ammonio-bromide of Cadmium 62
Ammonio-bromate of Cadmic Oxide 63
Ammonio-chloride of Cadmium 63
Chloride of Cadmium and Ammonium 63

Cadmium and Potassium.

Sulphate of Cadmic Oxide and Potash 63
Iodide of Cadmium and Potassium 64
Bromide of Cadmium and Potassium 64
Chloride of Cadmium and Potassium 64

Cadmium and Sodium.

Cadmium with Fluxes 64
Chloride of Cadmium and Sodium 64

Cadmium and Calcium.

Hypophosphite of Cadmic Oxide and Lime ? 64

Cadmium and Silicium.

Hydrated Silico-fluoride of Cadmium 64

Cadmium and Tungsten.

Tungstate of Cadmic Oxide.
a. Monotungstate.—*b*. Bitungstate 65
Sulphostungstate of Cadmium.—Cds,WS^6 65

Cadmium and Molybdenum.

Molybdate of Cadmic Oxide 65

Page

Sulphomolybdate of Cadmium 65
Persulphomolybdate of Cadmium 65

Cadmium and Vanadium.

Vanadiate of Cadmic Oxide.
a. Monovanadiate.—*b.* Bivanadiate 65

Cadmium and Arsenic.

Sulpharsenite of Cadmium 65
Sulpharseniate of Cadmium 66

Cadmium and Antimony.

Sulphantimoniate of Cadmium 66

Cadmium and Tellurium.

Sulphotellurite of Cadmium 66

Other Compounds of Cadmium 66

CHAPTER XXX. TIN.

Memoirs, &c., relating to Tin 66
History.—Sources 66
Preparation on the large scale.—Properties 67

COMPOUNDS OF TIN.

Tin and Oxygen.

Stannous Oxide—SnO 68
Hydrate of Stannous Oxide 69
Salts of Stannous Oxide, *or* Stannous Salts 69
Oxides of Tin intermediate between SnO and SnO^2.
a. Sesquioxide.—Sn^2O^3 70
b. Anomalous Stannate of Stannic Oxide 71
Stannic Oxide.—Stannic Acid.—SnO^2 71
Anomalous Hydrate of Stannic Acid 73
Ordinary Hydrate of Stannic Acid.... 74
Salts of Stannic Oxide, *or* Stannic Salts.
a. Anomalous Stannic Salts 74
β. Ordinary Stannic Salts 75
Salts of Stannic Acid; Stannates.
a. Anomalous Stannates 76
β. Ordinary Stannates.... 76

Tin and Boron.

Borate of Stannous Oxide 77

Tin and Phosphorus.

Phosphide of Tin 77
Phosphate of Stannous Oxide 77
Phosphite of Stannic Oxide 77
Phosphate of Stannous Oxide 78

Page

Tin and Sulphur.

Stannous Sulphide, *or* Sulphostannous Acid.—SnS 78
Hydrosulphate of Stannous Oxide 78
Sesquisulphide of Tin.—Sn^2S^3 79
Hydrated Sesquisulphide 79
Stannic Sulphide, *or* Sulphostannic Acid.—SnS^2.
Bi-hydrosulphate of Stannous Oxide 80
Tetrathionate of Stannous Oxide.... 81
Hyposulphite of Stannous Oxide 81
Sulphite of Stannous Oxide 81
¶ Hyposulphate of Stannous Oxide? 81
Sulphate of Stannous Oxide.
a. Basic Sulphate.—*b*. Monosulphate 81
Sulphate of Stannic Oxide.
a. Ordinary.—*b*. Anomalous 82
Stannous and Stannic Sulphocarbonates 82

Tin and Selenium.

Selenide of Tin 82
Selenite of Stannic Oxide 82

Tin and Iodine.

Stannous Iodide, *or* Iodostannous Acid.—SnI 82
¶ Stannic Iodide, *or* Iodostannic Acid.—SnI^2 83
Stannous and Stannic Iodates 83

Tin and Bromine.

Stannous Bromide, *or* Bromostannous Acid.—SnBr.... 84
Hydrobromate of Stannous Oxide 84
Stannic Bromide, *or* Bromostannic Acid.—$SnBr^2$ 84
Bromate of Stannous Oxide 84

Tin and Chlorine.

Stannous Chloride, *or* Chlorostannous Acid.—SnCl 84
Mono-hydrochlorate of Stannous Oxide; *Tin-salt* 85
Hydrated Stannous Oxychloride.—SnCl,SnO + 3Aq. 87
Hydrochlorate of Sesquioxide of Tin 87
Stannic Chloride, *or* Chlorostannic Acid.—$SnCl^2$.
Crystallized Hydrochlorate of Stannic Oxide 88
Aqueous Hydrochlorate of Stannic Oxide.
a. Ordinary.—*b*. Anomalous 89
Stannic Chloride with Sulphur and Phosphorus 89
Chlorostannate of Phosphuretted Hydrogen 89
Stannic Chloride with Terchloride of Phosphorus 90
Chlorosulphide of Tin.—SnS^2,$2SnCl^2$ 90
Chloride of Sulphur and Tin 90
Sulphate of Stannic Chloride 91
¶ Iodochloride of Tin.—SnCl,SnI 91

Tin and Fluorine.

Hydrofluate of Stannous Oxide 92
Hydrofluate of Stannic Oxide 92

Page

Tin and Nitrogen.

Nitrate of Stannous Oxide 92
Nitrate of Stannic Oxide 92
Nitric Oxide with Stannic Chloride 93
Stannate of Ammonia 93
Sulphostannate of Ammonium 93
Ammonio-protiodide of Tin.—$2NH^3,SnI$ 93
Iodostannite of Ammonium.—$NH^4I,2SnI$ 93
Ammonio-protochloride of Tin.—$NH^3,2SnCl$ 93
Ammonio-bichloride of Tin.—$NH^3,SnCl^2$ 93
Chlorostannite of Ammonium.—$NH^4Cl,SnCl+Aq.$ 94
Chlorostannate of Ammonium; *Pink-salt*.—$NH^4Cl,SnCl^2$ 94
Hydrochlorate and Stannite of Ammonia 95
Nitrate of Stannic Oxide and Ammonia.... 95

Tin and Potassium.

Alloy of Tin and Potassium 95
Stannite of Potash 95
Stannate of Potash.
a. Ordinary Stannate.
a. Monostannate 95
β. Acid Salt 96
b. Anomalous Stannate; Fremy's Metastannate of Potash 96
Sulphostannate of Potassium.—KS,Sn,S^2 96
Iodostannite of Potassium.—$KI,2SnI$ 97
Chlorostannite of Potassium.—$2KCl,SnCl+3$ Aq.
Chlorostannate of Potassium.—$KCl,SnCl^2$ 97
Hydrochlorate and Stannite of Potash 98

Tin and Sodium.

Alloy of Tin and Sodium 98
Stannite of Soda 98
Stannate of Soda: *a*. Ordinary.—*b*. Anomalous 98
Sulphostannate of Sodium 98
Iodostannite of Sodium 98
Chlorostannate of Sodium 98
Hydrochlorate and Stannite of Soda 99

Tin and Barium.

Stannate of Baryta 99
Sulphostannate of Barium 99
Iodostannite of Barium 99
¶ Chlorostannite of Barium.—$BaCl,SnCl+4Aq.$ 99
¶ Chlorostannate of Barium.—$BaCl,SnCl^2+5Aq.$ 99
Hydrochlorate and Stannite of Baryta 99

Tin and Strontium.

Stannate of Strontia 99
Sulphostannate of Strontium 99
Iodostannite of Strontium 99

Page

¶ Chlorostannite of Strontium.—$SrCl,SnCl+4Aq$.
¶ Chlorostannate of Strontium.—$SrCl,SnCl^2+5Aq$. 99
Hydrochlorate and Stannite of Strontia.... 99

Tin and Calcium.

Stannate of Zinc 100
Sulphostannate of Calcium 100

Tin and Magnesium.

Stannate of Magnesia.... 100
¶ Chlorostannate of Magnesium.—$MgCl,SnCl^2+5Aq$.... 100
Hydrochlorate and Stannite of Magnesia 100

Tin and Silicium.

Silicide of Tin 100
Silicofluoride of Tin 100

Tin and Tungsten.

Tungstate of Stannous Oxide 100
Stannous Sulphotungstate.—SnS, WS^3 101
Stannic Sulphotungstate.—SnS^2, WS^3 101

Tin and Molybdenum.

Molybdate of Stannic Oxide 101
Stannous Sulphomolybdate 101
Stannic Sulphomolybdate 101
Stannous Persulphomolybdate 101
Stannic Persulphomolybdate 101

Tin and Chromium.

Stannate of Chromic Oxide ? 101
Chromate of Stannous Oxide 102
Chromate of Stannic Oxide 102

Tin and Manganese.

Stannate of Manganous Oxide 102

Tin and Arsenic.

Arsenide of Tin.
Arsenite of Stannic Oxide, or Arseniate of Stannous Oxide? 102
Stannous Sulpharsenite 102
Stannic Sulpharsenite 102
Stannous Sulpharseniate 103
Stannic Sulpharseniate 103
Bichloride of Tin with Terchloride of Arsenic 103

Tin and Antimony.

Antimonide of Tin 103
Antimoniate of Stannic Oxide 103
Stannous Sulphantimoniate.... 104

Page

Tin and Tellurium.

Telluride of Tin 104
Stannous Sulpothellurite 104
Stannic Sulphotellurite 104

Tin and Bismuth.

Alloys of Tin and Bismuth 104
Alloy of Antimony, Bismuth and Tin 104

Tin and Zinc.

Alloys of Tin and Zinc 105
Stannate of Zinc-oxide 105

Other Compounds of Tin 105

Chapter XXXI. LEAD.

Memoirs, &c.—History.—Sources 105
Preparation on the large scale.—Purification.—Properties 106

Compounds of Lead.

Lead and Oxygen.

Suboxide of Lead.—Pb^2O ? 107
Lead-oxide.—PbO 108
Hydrate of Lead-oxide 113
Aqueous Solution of Lead-oxide 114
Lead-salts 115
Red Oxide of Lead.—Pb^3O^4 118
Sesquioxide of Lead ?—Pb^2O^3 120
Peroxide of Lead.—PbO^2 120

Lead and Carbon.

Carbide of Lead ? 122
Carbonate of Lead-oxide.
a. Bibasic Carbonate 122
b. Sesquibasic Carbonate: *White Lead* 123
c. Monobasic Carbonate : *Lead-spar* 126
d. Five-fourths Carbonate 127
e. Acid Carbonate 127

Lead and Boron.

Borate of Lead-oxide 128

Lead and Phosphorus.

Phosphide of Lead 128
Hypophosphite of Lead-oxide 128
Phosphite of Lead-oxide.
a. Quadrobasic.—*b.* Bibasic 129

Page

Phosphate of Lead-oxide.
a. Terbasic.—*b.* Bibasic 130
c. 3 At. Acid to 4 At. Base.—*d.* With excess of Acid 131
Pyrophosphate of Lead-oxide, ... 131
Metaphosphate of Lead-oxide 131

Lead and Sulphur.

One-fourth Sulphide of Lead 132
Disulphide of Lead 132
Protosulphide of Lead : *Galena* 132
Pentasulphide of Lead 134
Hyposulphite of Lead-oxide 135
Tetrathionate of Lead-oxide 135
Trithionate of Lead-oxide 135
Sulphite of Lead-oxide 135
Hyposulphate of Lead-oxide.
a. Terbasic.—*b.* Bibasic ?—*c.* Monobasic 135
Sulphate of Lead-oxide.
a. Basic.—*b.* Monobasic : *Lead-vitriol* 136
Sulphate and Carbonate of Lead-oxide : *Leadhillite*.... 138
Sulphocarbonate of Lead 138

Lead and Selenium.

Selenide of Lead 139
Selenite of Lead-oxide.
a. Basic.—*b.* Monobasic 139
Seleniate of Lead-oxide 140

Lead and Iodine.

Iodide of Lead 140
Oxy-iodide of Lead.
a. PbI, PbO 141
b. PbI, 2PbO 142
Iodide of Lead and Hydrogen 142
Basic Periodite of Lead-oxide ?
a. Blue Salt.—*b.* Violet Salt 143
Iodate of Lead-oxide 143
Periodate of Lead-oxide 144

Lead and Bromine.

Bromide of Lead 144
Oxybromide of Lead 144
Bromate of Lead-oxide 145
Bromo-carbonate of Lead 145

Lead and Chlorine.

Chloride of Lead: *Plumum corneum; Cotunnite* .... 14[illegible]
Oxychloride of Lead.
a. 3PbCl, PbO—*b.*PbCl, PbO. .... 1[illegible]
c. PbCl, 2PbO : *Mendipite* .... 1[illegible]
d. PbCl, 3PbO.—*e.* PbCl, 5PbO.—*f. Cassel-yellow* 1[illegible]

Page

Chlorite of Lead-oxide 148
Chlorate of Lead-oxide 148
Perchlorate of Lead-oxide 148
Chlorocarbonate of Lead : *Horn-lead* 148
Chlorophosphite of Lead 149
Chlorophosphate of Lead : *Pyromorphite* 149
Chlorosulphide of Lead 150
Chlorosulphate of Lead 150
Chloriodide of Lead 151

Lead and Fluorine.

Fluoride of Lead 151
Oxyfluoride of Lead 151
Borofluoride of Lead.—PbF, BF^3 151
Chlorofluoride of Lead.—PbCl, PbF 151

Lead and Nitrogen.

Nitrite of Lead-oxide.
a. Quadrobasic 152
¶ *b.* Terbasic ?—¶ *c.* Bibasic.—*d.* Monobasic 153
Hyponitrate of Lead-oxide.
a. Quadrobasic ? 153
b. Bibasic 154
Nitrate of Lead-oxide
a. Sexbasic.—*b.* Terbasic 156
c. Bibasic.—*d.* Monobasic 157
Boronitrate of Lead ? 158
Phosphonitrate of Lead-oxide 158
¶ Azophosphate of Lead-oxide 158
Nitrate of Lead-oxide with Fluoride of Lead 158
Plumbite of Ammonia 158
Hyposulphite of Lead-oxide and Ammonia 158
Sulphate of Lead-oxide and Ammonia 159
Ammonio-iodide of Lead 159
Iodide of Lead and Ammonium 159
Ammonio-chloride of Lead 159
Chloride of Lead and Ammonium 160

Lead and Potassium.

Alloy of Lead and Potassium 160
Plumbite of Potash 160
Plumbate of Potash 160
Hyposulphite of Lead-oxide and Potash 160
Sulphate of Lead-oxide and Potash 161
Iodide of Lead and Ammonium.
a. 2KI, PbI^2.—*b.* 2KI,3PbI 161
Bromide of Lead and Potassium 162

Lead and Sodium.

Alloy of Lead and Sodium 162

Page

Plumbite of Soda 162
Plumbate of Soda 162
Carbonate of Lead-oxide and Soda 162
Sulphide of Lead and Sodium 162
Hyposulphite of Lead-oxide and Soda 162
Sulphate of Lead-oxide and Soda.... 163
Iodide of Lead and Sodium 163
Bromide of Lead and Sodium 163
Chloride of Lead and Sodium 163

Lead and Barium.

Plumbite of Baryta 163
Sulphide of Lead and Barium 163
Hyposulphite of Lead-oxide and Baryta 163
Chloride of Lead and Barium 163

Lead and Strontium.

Hyposulphite of Lead-oxide and Strontia 164

Lead and Calcium.

Plumbite of Lime 164
Carbonate of Lead-oxide and Lime: *Plumbo-calcite* 164
Hyposulphite of Lead-oxide and Lime.... 164
Phosphate of Lead-oxide and Lime with Chloride of Lead 164
Sulphate of Lead-oxide with Fluorspar 164

Lead and Aluminum.

Phosphate of Lead-oxide with Hydrate of Alumina: *Plombgomme* 165

Lead and Silicium.

Silicide of Lead 165
Silicate of Lead-oxide 165
Borosilicate of Lead-oxide 165
Silicofluoride of Lead 166
Silicate of Lead-oxide and an Alkali.
a. Lead-glass.—*b.* Containing a large proportion of alkali 166
Silicate of Zirconia and Lead-oxide.
a. $2PbO,2ZrO,SiO^2$.—*b.* $PbO,2ZrO,SiO^2$ 166

Lead and Titanium.

Fluoride of Titanium and Lead 166

Lead and Tantalum.

Fluoride of Tantalum and Lead 166

Lead and Tungsten.

Tungstide of Lead 166
Tungstate of Lead-oxide.—*a.* Monotungstate: *Scheelitine* 166
b. Bitungstate 167
Sulphotungstate of Lead: PbS,WS^3 167

Page

Lead and Molybdenum.

Molybdide of Lead 167
Molybdate of Lead-oxide : *Yellow Lead-ore* 167
Sulphomolybdate of Lead 168
Persulphomolybdate of Lead 168

Lead and Vanadium.

Vanadiate of Lead-oxide.
a. Monovanadiate.—*b.* Bivanadiate 168
Vanadite 169

Lead and Chromium.

Chromate of Lead-oxide.
a. Dichromate : *Chrome-red* 169
b. Sesquibasic Chromate : *Melanochroite* 170
c. Monochromate: *Red Lead-spar; Chrome-yellow* 170

Lead and Uranium.

Uranate of Lead-oxide.—$PbO,2U^2O^3$ 172

Lead and Manganese 172

Lead and Arsenic.

Arsenide of Lead 172
Arsenite of Lead-oxide.
a. Bibasic.—*b.* Monobasic 173
Arseniate of Lead-oxide.
a. Terbasic.—*b.* Bibasic 173
Sulpharsenite of Lead.—$2PbS,AsS^3$ 174
Sulpharseniate of Lead 174
Arseniate of Lead-oxide with Chloride of Lead 174
Arsenide of Lead and Potassium 174

Lead and Antimony.

Antimonide of Lead.—*a.* Pb^{18},Sb^3 174
b. Pb^4Sb.—*Type-metal* 175
Antimoniate of Lead-oxide : *Naples Yellow* 175
Sulphantimonite of Lead.
a. Sexbasic *Kilkbrickenite* 175
b. Quintobasic *Geocronite.*—*c.* Terbasic : *Boulangerite* 176
d. Bibasic *Feather-ore.*—*e.* Sesquibasic : *Jamesonite* 176
f. Four-thirds-basic *Plagionite* 176
g. Monobasic *Zinkenite* 177
Sulphantimoniate of Lead 177

Lead and Tellurium.

Telluride of Lead 177
Tellurite of Lead-oxide 178
Tellurate of Lead-oxide 178
Sulphotellurite of Lead 178

Page

Lead and Bismuth.

Alloy of Lead and Bismuth 178
Sulphobismuthate of Lead.—$3PbS,BiS^3$: *Kobellite* 179

Lead and Zinc.

Alloy of Lead and Zinc 179

Lead and Tin.

Alloys of Lead and Tin 179
Stannate of Lead-oxide 180
Antimonide of Lead and Tin 180
Alloys of Bismuth, Lead and Tin 180
Alloys of Lead, Tin and Zinc 181

Other Compounds of Lead 181

CHAPTER XXXII. IRON.

Memoirs, &c.—History.—Sources.—Preparation on the large scale 182
Purification.—Properties 183

COMPOUNDS OF IRON.

Iron and Oxygen.

Oxidation of Iron 184
Suboxide of Iron.—Fe^4O ? 187
Ferrous Oxide.....FeO 187
Hydrate of Ferrous Oxide 187
Ferrous Salts :—*Proto-salts of Iron* 188
Ferroso-ferric Oxide.
a. Scale-oxide : $6FeO, Fe^2O^3$.—*b.* Magnetic Oxide : Fe^3O^4 or FeO,Fe^2O^3 190
Hydrate of Ferroso-ferric Oxide.
a. Dingy green Hydrate.—*β.* Black Hydrate 192
Ferroso-ferric Salts 194
Ferric-oxide.—Fe^2O^3 194
Hydrate of Ferric-oxide : Brown Iron-ore 196
a. Fe^2O^3,HO: *Needle Iron-ore ; Göthite ; Lepidokrokite ; Pseudomorphous Brown Iron-ore* 197
β. $2Fe^2O^3,3HO$: *Brown Hæmatite* 197
γ. $Fe^2O^3,2HO$ 198
Ferric Salts : *Per-salts of Iron* 198
Ferric Acid.—FeO^3 ? 201

Iron and Hydrogen.

Ferruretted Hydrogen gas ? 201

Iron and Carbon.

Carbide of Iron 202
a. Bar or Wrought Iron 205

Page

b. Steel 206
c. Cast-iron or Pig-iron 210
A. White Pig-iron 211
B. Grey Pig-iron 212
d. Pure or Saturated Cast-iron: Fe^4C 219
Carbonate of Ferrous Oxide.
a. Monobasic: *Iron-spar* or *Spathic Iron-ore*; *Spharo-siderite*; *Junkerite*.... 219
b. Acid Carbonate 221
Carbonate of Ferric Oxide ? 222

Iron and Boron.
Borate of Ferrous Oxide 222
Borate of Ferric Oxide 222

Iron and Phosphorus.
Phosphide of Iron.—*a.* Fe^4P 222
b. Fe^3P^2 223
Hypophosphite of Ferric Oxide 223
Hypophosphate of Ferric Oxide 223
Phosphite of Ferrous Oxide 223
Phosphite of Ferric Oxide 223
Phosphate of Ferrous Oxide.
a. Terbasic: *Blue Iron-ore* or *Vivianite* 224
b. Bibasic.—*c.* Acid Phosphate 225
¶ Pyrophosphate of Ferrous Oxide 225
Phosphate of Ferric Oxide.
a. Polybasic: *Limonite* 225
b. Bibasic 225
c. Sesquiphosphate 226
d. Biphosphate ? 226
¶ Pyrophosphate of Ferric Oxide 227
¶ Metaphosphate of Ferric Oxide 227

Iron and Sulphur.
One-eighth Sulphide of Iron 227
Disulphide of Iron 227
Protosulphide of Iron, or Ferrous Sulphide 228
Hydrosulphate of Ferrous Oxide 230
Eight-sevenths Sulphide of Iron: *Magnetic Pyrites* 230
Sesquisulphide of Iron, or Ferric Sulphide 231
Hydrosulphate of Ferric Oxide 232
Bisulphide of Iron: *Iron Pyrites* 232
Sulphide of Ferrous Oxide ? 235
Hyposulphite of Ferrous Oxide 235
Sulphite of Ferrous Oxide 236
Sulphite of Ferric Oxide 236
Hyposulphate of Ferrous Oxide 236
Hyposulphate of Ferric Oxide 237
Sulphate of Ferrous Oxide: *Protosulphate of Iron, Green Vitriol, Copperas* 237

Page
a. Mono-hydrated.—*β.* Bi-hydrated.—*γ.* Ter-hydrated.... 239
δ. Tetra-hydrated.—*ε.* Hepta-hydrated 239
Sesquisulphate of Ferrous Oxide? 241
Sulphate of Ferric Oxide.
a. Sex-basic 241
b. Quadrobasic.—*c.* Terbasic 242
d. Bibasic: *Vitriol-ochre* 242
e. Monobasic 243
f. Sesquisulphate: *Fibroferrite* 243
g. Bisulphate 243
h. Tersulphate; Normal Ferric Sulphate 244
Coquimbite 245
Ferrous Sulphocarbonate 245
Ferric Sulphocarbonate 246
Ferrous Hyposulphophosphite.—FeS,PS 246
Ferrous Sulphophosphite.—$2FeS,PS^3$.
Phosphosulphate of Ferric Oxide: *Diadochite*
$(Fe^2O^3,2PO^5+8Aq.)+4(Fe^2O^3,SO^3+6Aq.)$ 246

Iron and Selenium.
Selenide of Iron 246
Selenite of Ferrous Oxide.
a. Monoselenite.—*b.* Biselenite 247
Selenite of Ferric Oxide.
a. Sesquiselenite.—*b.* Terselenite.—*c.* Sexselenite 247

Iron and Iodine.
Protiodide of Iron 247
Hydriodate of Ferrous Oxide 248
Iodate of Ferrous Oxide? 249
Iodate of Ferric Oxide.
a. Basic Iodate 249
b. Biniodate 250
Ferrous and Ferric Periodates 250

Iron and Bromine.
Protobromide of Iron, *or* Ferrous Bromide 250
Hydrobromate of Ferrous Oxide 250
Sesquibromide of Iron, *or* Ferric Bromide 250
Hydrobromate of Ferric Oxide 251
Ferric Oxybromide 251
Bromate of Ferric Oxide 251

Iron and Chlorine.
Protochloride of Iron, *or* Ferrous Chloride 251
Ter-hydrated Hydrochlorate of Ferrous Oxide.... 252
Sesquichloride of Iron, *or* Ferric Chloride 253
Ter-hydrochlorate of Ferric Oxide 254
a. Penta-hydrated 254
b. Dodeca-hydrated 255
Aqueous Ter-hydrochlorate of Ferric Oxide 255

Page

Ferric Oxychloride, or Basic Hydrochlorate of Ferric Oxide.
a. Soluble 255
b. Insoluble 256
Perchlorate of Ferrous Oxide 256

Iron and Fluorine.

Protofluoride of Iron, and Mono-hydrofluate of Ferrous Oxide 256
Sesquifluoride of Iron, and Ter-hydrofluate of Ferric Oxide 256
Ferric Oxyfluoride, or Basic Hydrofluate of Ferric Oxide 257

Iron and Nitrogen.

Nitride of Iron 257
Nitrate of Ferrous Oxide 257
Nitrate of Ferric Oxide.
a. Acid Nitrate 258
b. Basic Nitrate 259
¶ Azophosphate of Ferric Oxide 259
Ferrite of Ammonia ?.... 260
Carbonate of Ferric Oxide and Ammonia 260
Phosphate of Ferrous Oxide and Ammonia 260
Phosphate of Ferric Oxide and Ammonia 261
¶ Ammonio-azophosphate of Ferric Oxide 261
Sulphate of Ferrous Oxide and Ammonia 261
Sulphate of Ferric Oxide and Ammonia.
a. Basic.—*b.* Containing Bisulphate of Ferric Oxide.
c. Containing Tersulphate of Ferric Oxide 262
Hydrobromate of Ammonia containing Sesquibromide of Iron.... 262
Ammonio-protochloride of Iron 262
Protochloride of Iron and Ammonium, *or* Ferroso-ammonic Chloride 263
Ammonio-sesquichloride of Iron.—NH^3,Fe^2Cl^3 263
Sesquichloride of Iron and Ammonium, *or* Ferrico-ammonic Chloride : $2NH^4Cl+Fe^2Cl^3+2Aq.$ 263
Sal-ammoniac containing Sesquichloride of Iron 264

Iron and Potassium.

Alloy of Iron and Potassium 264
Ferrite of Potash 265
Ferrate of Potash 265
Carbonate of Ferric Oxide and Potash 268
Boride of Iron and Potassium 268
Sulphide of Iron and Potassium 268
Sulphate of Ferrous Oxide and Potash 268
Sulphate of Ferric Oxide and Potash.
a. $KO,SO^3+4(Fe^2O^3,SO^3)+9Aq.$: *Yellow Iron-ore* 268
b. $KO,SO^3+3(2Fe^2O^3,3SO^3)+18Aq.$ 269
c. $2(KO,SO^3)+Fe^2O^3,2SO^3+6Aq.$.... 269

Page

d. $2(KO,SO^3)+3(Fe^2O^3,2SO^3)+22Aq.$ 269
e. $KO,SO^3+Fe^2O^3,3SO^3+24Aq.$ *Potash Iron-alum* 270
Protochloride of Iron and Potassium, *or* Ferroso-potassic Chloride 271
Sesquichloride of Iron and Potassium, *or* Ferrico-potassic Chloride 271
Protofluoride of Iron and Potassium, *or* Ferroso-potassic Fluoride 271
Sesquifluoride of Iron and Potassium, *or* Ferrico-potassic Fluoride.
a. Terbasic: $3KF,Fe^2F^3$.—*b.* Bibasic: $2KF,Fe^2F^3$ 271

Iron and Sodium.

Ferrite of Soda 271
Carbonate of Ferric Oxide and Soda 272
Iron with Fluxes 272
¶ Pyrophosphate of Ferrous Oxide and Soda 272
¶ Pyrophosphate of Ferric Oxide and Soda 272
Sulphide of Iron and Sodium 272
Basic Sulphate of Ferric Oxide and Soda 273

Iron and Barium.

Alloy of Iron and Barium 273
Ferrate of Baryta 273
Sulphide of Iron and Barium 273

Iron and Calcium.

Hyposulphite of Ferric Oxide and Lime 274
Sulphide of Iron and Calcium 274

Iron and Magnesium.

Alloy of Iron and Magnesium 274
Carbonate of Ferrous Oxide and Magnesia 274
Sulphate of Ferroso-ferric Oxide and Magnesia: *Botryogene* 274

Iron and Cerium.

Carbide of Iron and Cerium 274

Iron and Glucinum.

Alloy of Iron and Glucinum 274
Carbide of Iron and Glucinum 275

Iron and Aluminum.

Alloy of Iron and Aluminum 275
Aluminate of Ferrous Oxide; *Zeilanite; Chlorospinelle* 275
Carbide of Iron and Aluminum 276
Sulphate of Alumina and Ferrous Oxide: *Feather-salt.*
a. $6(FeO,SO^3)+Al^2O^3,2SO^3+48Aq.$ 276
b. $2(FeO,SO^3)+Al^2O^3,3SO^3+27Aq.$: *Bergbutter* 276
c. $FeO,SO^3+Al^2O^3 3SO^3+24Aq.$ 276

Page

d. $MgO,SO^3 + FeO,SO^3 + Al^2O^3,SO^3 + 15Aq.$ 277
Sulphite of Alumina and Ferric Oxide 277

Iron and Silicium.

Silicide of Iron.... 277
Silicate of Ferrous Oxide.
a. Disilicate: *Hyalosiderite; Fayalite* 278
Knebelite; FeO,MnO,SiO^2 279
b. Monosilicate: *Pyrosmalite* 279
c. Six-fifths Silicate: *Hornblendes rich in Iron.*
a. Arfvedsonite.—*β. Aegyrine* 280
d. Five-fourths Silicate: *Krokydolite* 281
e. Quadrosilicate 281
Silicate of Ferric Oxide.
a. Monosilicate 281
b. Sesquisilicate: *Yellow Earth* 282
c. Bisilicate: *Hisingerite* 282
d. Tersilicate: *Nontronite* 282
e. Quadrosilicate: *Anthosiderite* 283
Silicate of Ferric Oxide with Carbonate of Soda.
a. Bibasic: *Glauber's Iron-tree* 283
b. With 4 atoms of Acid 284
Double Silicates containing Ferric Oxide and Alumina, on the one hand, and Ferrous Oxide with others of the stronger bases, on the other.
Chamoisite.—$2(5FeO,SiO^2) + Al^2O^3,3SiO^2 + 12Aq.$ 284
Pea-ore.—$10FeO,3SiO^2 + Al^2O^3,SiO^2 + 5Aq.$ 284
Stilpnomelane.—$9(FeO,SiO^2) + Al^2O^3,3SiO^2 + 7Aq.$ 285
Gedrite.—$8FeO,6SiO^2 + Al^2O^3,SiO^2 + Aq.$? 285
Ilvaite.—$2(2FeO,SiO^2) + Fe^2O^3,SiO^2$ 285
Cronstedtite.—$3FeO,SiO^2 + Fe^2O^3SiO^2 + 3Aq.$ 286
Wichtyn.—$3(FeO,SiO^2) + Al^2O^3,SiO^2$ 286
Achmite.—$NaO,2SiO^2 + FeO,SiO^2 + FeO,3SiO^2$ 286
Ottrelite.—$3(FeO,SiO^2) + 2Al^2O^3,3SiO^2 + 3Aq.$ 287
Chlorite-spar.—$2(FeO,SiO^2) + 2Al^2O^3,SiO^2$ 287
Lepidomelane.—$(KO;FeO)SiO^2 + (Fe^2O^3;Al^2O^3)SiO^2$ 287
Pinguite.—$FeO,2SiO^2 + 2(Fe^2O^3,2SiO^2) + 14Aq.$? 287
Glass-fluxes containing Ferrous and Ferric Oxide 288
Carbide of Silicium and Iron 288
Protofluoride of Iron and Silicium.—FeF,SiF^4.... 288
Sesquifluoride of Iron and Silicium.—$Fe^2F^6,3SiF^4$ 288

Iron and Titanium.

Titanide of Iron? 289
Titanate of Ferrous Oxide: *Titaniferous Iron.*
a. Ilmenite 289
β. Kibdelophane 290
γ. Basanomelane 291

Page

Titanate of Ferric Oxide 292
Bifluoride of Titanium with Sesquifluoride of Iron.... 292

Iron and Tantalum.

Tantalide of Iron 292
Tantalite of Ferrous Oxide: *a variety of Tantalite* 292
Tantalate of Ferric Oxide.
a. Bibasic: *Columbite*.... 292
b. Monobasic: *Ordinary Tantalite* 293

Iron and Tungsten.

Tungstate of Ferrous Oxide.
a. Monotungstate.—*Wolfram* 294
b. Bitungstate 296
Carbide of Tungsten and Iron 297
Ferrous Sulphotungstate : FeS,WS^3 297
Ferric Sulphotungstate : $Fe^2S^3,3WS^3$.... 297

Iron and Molybdenum.

Molybdide of Iron 297
Molybdate of Ferric Oxide 297
Ferrous Sulphomolybdate 297
Ferric Sulphomolybdate 298
Ferrous Persulphomolybdate 298
Ferric Persulphomolybdate 298

Iron and Vanadium.

Vanadiate of Ferrous Oxide ?
Vanadiate of Ferric Oxide.

Iron and Chromium.

Chromic Oxide with Ferrous Oxide : *Chrome-iron-ore* 298
Chromic Oxide with Ferric Oxide 299
Chromate of Ferric Oxide.
a. Basic.—*b.* With 4 atoms of acid 299
Carbide of Chromium and Iron 300

Iron and Uranium.

Uranide of Iron ? 300

Iron and Manganese.

Manganide of Iron 300
¶ Manganiferous Magnetic Iron-ore : $(FeO,MnO)Fe^2O^3$ 300
Carbide of Manganese and Iron 301
Phosphate of Manganous Oxide and Ferrous Oxide.
a. Quadrobasic: *Triplite*.—$4MnO,PO^5+FeO,PO^5$ 301
b. Terbasic.
α. Triphyline.—$3(\frac{9}{15}LiO,\frac{1}{15}MnO,\frac{5}{15}FeO)PO^5$ 301
β. Tetraphyline or *Perowskine*.—$3(\frac{7}{24}LiO,\frac{1}{24}MgO,\frac{4}{24}MnO,\frac{12}{24}FeO)PO^5$ 302

Page

γ: *Iron-apatite.*—$3MnO,PO^5+2(3FeO,PO^5)FeF$ 302

c. 5 atoms of Base to 2 atoms of Acid.

α. *Hetepozite.*—$5(MnO;FeO)2PO^5+2Aq.$ 303

β. *Haraulite.*—$5(MnO;FeO)2PO^5+8Aq.$ 303

Phosphate of Ferric Oxide and Manganic Oxide; *Weathered Triphyline*, or *Triplite of Bodenmais* 303

Iron and Arsenic.

Arsenide of Iron.

a. Di-arsenide 303

b. Mono-arsenide: *Arsenical Iron* or *Arsenical Pyrites* 304

Arsenite of Ferrous Oxide 304

Arsenite of Ferric Oxide.

a. Quadrobasic Arsenite 304

b. Sesqui-arsenite? 305

Arseniate of Ferrous Oxide.

a. Terbasic.—b. Bibasic 305

c. Acid Salt 306

Ferroso-ferric Arseniate.

a. *Cube-ore.*—b. *Skorodite* 306

Arseniate of Ferric Oxide.

a. Sixteen-basic.—b. Bibasic.—c. Sesqui-arseniate 307

Arsenio-sulphate of Ferric Oxide: *Pittizite* 308

Arseniate of Ferric Oxide and Lime: *Arseniosiderite* 309

Ferrous Sulpharsenite 309

Ferric Sulpharsenite 309

Ferrous Sulpharseniate 309

Ferric Sulpharseniate 309

Proto-arsenide of Iron with Bisulphide of Iron: *Mispickel.*

$FeAs,FeS^2$ 309

Iron and Antimony.

Antimonide of Iron 310

Ferrous Antimonite 310

Ferrous Antimoniate? 310

Ferrous Sulphantimonite: *Berthierite* or *Haidingerite.*

a. $3FeS,2SbS^3$.—b. FeS,SbS^3.—c. $3FeS,4SbS^3$ .... 31.

Ferrous Sulphantimoniate? 311

Antimonide of Iron and Potassium 312

Iron and Tellurium.

Telluride of Iron 312

Ferrous Tellurite 312

Ferric Tellurite 312

Ferrous Tellurate 312

Ferric Tellurate 312

Ferrous Sulphotellurite 312

Ferric Sulphotellurate 312

Iron and Bismuth.

Bismuthide of Iron 312

Page

Bismuthide of Iron and Potassium 312

Iron and Zinc.

Alloy of Iron and Zinc 312

Ferric Oxide with Zinc-oxide: *Franklinite.* — $(ZnO;FeO),(Mn^2O^3;Fe^2O^3)$ 313

Carbide of Iron and Zinc 314

Sulphate of Ferrous Oxide and Zinc Oxide.

Sulphate of Ferrous Oxide, Zinc-oxide and Ammonia 314

Iron and Tin.

Alloy of Iron and Tin 314

Carbide of Iron and Tin 315

Iron and Lead.

Alloy of Iron and Lead 315

Other Compounds of Iron 315

Chapter XXXIII. COBALT.

Memoirs, &c.—History.—Sources.—Preparation .. 316

Special Modes of Separation from particular Metals.

a. From Nickel 319

b. From Manganese 321

Properties of Cobalt 322

Compounds of Cobalt.

Cobalt and Oxygen.

Cobalt-oxide or Cobaltous Oxide.—CoO 322

Hydrate of Cobalt-oxide 323

Cobalt-salts 324

Cobaltoso-Cobaltic Oxide.

a. $Co^8O^9=6CoO,Co^2O^3$.—*b.* $CO^6O^7=4CoO,Co^2O^3$ 326

c. $Co^3O^4=CoO,Co^2O^3$ 326

Cobaltic Oxide.—Co^2O^3 326

Hydrate of Cobaltic Oxide 327

Cobaltic Salts 328

Cobaltic Acid?—CoO^3 328

Cobalt and Carbon.

Carbonate of Cobalt-oxide.... 328

Cobalt and Boron.

Borate of Cobalt-oxide 329

Cobalt and Phosphorus.

Phosphide of Cobalt.

a. With a very large excess of Cobalt 329

b. Triphosphide 329

Hypophosphite of Cobalt-oxide 330

Phosphite of Cobalt-oxide 330

Page

Ordinary Phosphate of Cobalt-oxide.—*Terbasic* 330
Pyrophosphate of Cobalt-oxide 331
¶ Metaphosphate of Cobalt-oxide 331

Cobalt and Sulphur.

Protosulphide of Cobalt 331
Hydrosulphate of Cobalt-oxide 331
Oxysulphide of Cobalt 322
Sesquisulphide of Cobalt: *Cobalt-pyrites* 332
Bisulphide of Cobalt 332
Hyposulphite of Cobalt-oxide 333
Sulphite of Cobalt-oxide 333
Hyposulphate of Cobalt-oxide 333
Sulphate of Cobalt-oxide.
a. Basic Sulphate.—*b.* Monosulphate: *Cobalt-vitriol* 333
Sulphocarbonate of Cobalt.... 334

Cobalt and Selenium.

Selenide of Cobalt 334
Selenite of Cobalt-oxide 334
Seleniate of Cobalt-oxide 334

Cobalt and Iodine.

Iodide of Cobalt.—CoI 335
Hydriodate of Cobalt-oxide 335
Oxy-iodide of Cobalt.—CoO,CoI ? 335
Iodide of Cobalt-oxide 335

Cobalt and Bromine.

Bromide of Cobalt.—CoBr.... 335
Hydrobromate of Cobalt-oxide 336
Bromate of Cobalt-oxide 336

Cobalt and Chlorine.

Chloride of Cobalt.—CoCl 336
Hydrochlorate of Cobalt-oxide 337
¶ Chlorate of Cobalt-oxide 337

Cobalt and Chlorine.

Fluoride of Cobalt, and Hydrofluate of Cobalt-oxide 337
Oxyfluoride of Cobalt.—2(CoO,CoF) + HO 338

Cobalt and Nitrogen.

Nitrate of Cobalt-oxide.
a. Sexbasic.—*b.* Monobasic 338
Carbonate of Cobalt-oxide and Ammonia 339
Cobalto-hyposulphate of Ammonia. — $3NH^3,Co^2O^3 + 2(NH^3,S^2O^5)$ 339
Ammonio-sulphate of Cobalt-oxide.—$3NH^3 + CoO,SO^3$ 339
Sulphate of Cobalt-oxide and Ammonia.—$NH^4O,SO^3 + CoO,SO^3 + 6Aq$. 340

Page

Ammonio-iodide of Cobalt.
a. Terbasic: $3NH^3,CoI$ 340
b. Bibasic: $2NH^3,CoI$ 340
Iodate of Cobalt-oxide and Ammonia 340
Ammonio-bromide of Cobalt.—$3NH^3,CoBr$ 340
Ammonio-sesquibromide of Cobalt? — $3Co^2O^3,2Co^2Br^3 + 15NH^3 + 20Aq$. 341
Cobalto-bromate of Ammonia? — $NH^3,Co^2O^3 + 6(NH^3,BrO^5) + 12Aq$..... 341
Ammonio-chloride of Cobalt.—$2NH^3,CoCl$ 342
Fluoride of Cobalt and Ammonium 342
Nitrate of Cobalt-oxide and Ammonia 342
Cobalto-nitrate of Ammonia 342

Cobalt and Potassium.
Cobaltite of Potash 343
Carbonate of Cobalt-oxide and Potash 343
Sulphate of Cobalt-oxide and Potash 344
Fluoride of Cobalt and Potassium 344

Cobalt and Sodium.
Cobaltite of Soda 344
Carbonate of Cobalt-oxide and Soda 344
Cobalt with Fluxes 344
¶ Metaphosphate of Cobalt-oxide and Soda 344

Cobalt and Calcium.
Hypophosphate of Cobalt-oxide and Lime 344

Cobalt and Magnesium.
Cobaltite of Magnesia.... 345

Cobalt and Aluminum.
Aluminate of Cobalt-oxide 345

Cobalt and Silicium.
Silicate of Cobalt-oxide 345
Hydrated Fluoride of Silicium and Cobalt 345
Cobalt-glass 346

Cobalt and Tungsten.
Tungstate of Cobalt-oxide.
a. Monotungstate.—*b.* Bitungstate 346
Sulphotungstate of Cobalt.—CoS,WS^3 346

Cobalt and Molybdenum.
Molybdate of Cobalt-oxide 347
Sulphomolybdate of Cobalt 347
Persulphomolybdate of Cobalt 347

Cobalt and Vanadium.
Vanadiate of Cobalt-oxide.
a. Monovanadiate.—*b.* Acid Vanadiate 34

Page

Cobalt and Chromium.

Chromate of Cobalt-oxide 347

Cobalt and Manganese.

Peroxide of Manganese with Protoxide of Cobalt.—*Earthy Cobalt* 347

Cobalt and Arsenic.

Arsenide of Cobalt.

a. 2 pts. Co with 3 pts. As.—*b.* 5(Fe;Co;Cu),As 483

c.—*Tin-white Cobalt, Cobaltine, Smaltine, Speiskobold:* (Co;Fe;Ni)As 348

d.—*Tesseral Pyrites:* Co^2As^3 349

Arsenite of Cobalt-oxide 349

Arseniate of Cobalt-oxide.

a. Terbasic; *Cobalt-bloom; Cobalt-coating* 349

b. Acid Arseniate 351

Sulpharsenite of Cobalt.—$2CoS,AsS^3$ 351

Sulpharseniate of Cobalt.—$2CoS,AsS^5$ 351

Sulphide of Cobalt with Arsenide of Cobalt: *Cobalt-glance.* $CoAs,CoS^2$ 351

Cobalt and Antimony.

Antimonide of Cobalt.... 353

Antimonite of Cobalt-oxide 353

Antimoniate of Cobalt-oxide 35

Sulphantimoniate of Cobalt 353

Cobalt and Tellurium.

Tellurite of Cobalt-oxide 353

Tellurate of Cobalt-oxide 353

Sulphotellurite of Cobalt 353

Cobalt and Zinc.

Alloy of Zinc and Cobalt 353

Cobalt-oxide with Zinc-oxide: *Rinman's Green* 353

Sulphate of Cobalt-oxide and Zinc-oxide 354

Cobalt and Tin.

Alloy of Cobalt and Tin 354

Stannate of Cobalt-oxide 354

Cobalt and Iron.

Alloy of Cobalt and Iron 354

Other Compounds of Cobalt 354

Page

Seleniate of Nickel-oxide 374

Nickel and Iodine.

Iodide of Nickel 374
Hydriodate of Nickel-oxide 375
Hydrated Oxy-iodide of Nickel ? 375
Iodate of Nickel-oxide 376

Nickel and Bromine.

Bromide of Nickel 376
Hydrobromate of Nickel-oxide 376
Bromate of Nickel-oxide 377

Nickel and Chlorine.

Chloride of Nickel 377
Hydrochlorate of Nickel-oxide 378
Hydrated Oxychloride of Nickel 378
Chlorate of Nickel-oxide 378

Nickel and Fluorine.

Fluoride and Oxyfluoride of Nickel 379

Nickel and Nitrogen.

Nitride of Nickel ? 379
Nitrate of Nickel-oxide.
a. Basic.—*b.* Mononitrate 379
Niccolate of Ammonia 379
Carbonate of Nickel-oxide and Ammonia.
a. With excess of Carbonate of Ammonia 379
b. With excess of Nickel-carbonate 380
Phosphate of Nickel-oxide and Ammonia 380
Hydrosulphate of Nickel-oxide and Ammonia 380
Ammonio-hyposulphite of Nickel-oxide. — $2NH^3 + NiO,S^2O^2 + 6Aq$. 380
Ammonio-hyposulphate of Nickel-oxide. — $3NH^3 + NiO,S^2O^5$ 380
Ammonio-sulphate of Nickel-oxide.—$3NH^3 + NiO,SO^3$ 381
Niccolo-sulphate of Ammonia.—$NH^4O,NiO + NH^4O,SO^3$ 381
Sulphate of Nickel-oxide and Ammonia.—$NH^4O,SO^3 + NiO,SO^3 + 6Aq$. 381
Ammonio-iodide of Nickel.
a. Terbasic.—$3NH^3,NiI$ 381
b. Bibasic.—$2NH^3,NiI$ 382
Niccolo-iodate of Ammonia.—$NH^3,NiO + NH^3,IO^5$? 382
Ammonio-bromide of Nickel.—$3NH^3,NiBr$ 382
Ammonio-bromate of Nickel-oxide 383
Ammonio-chloride of Nickel.—$3NH^3,NiCl$ 383
Chloride of Nickel and Ammonium.—$NH^4Cl,2NiCl + 12Aq$. 383
Fluoride of Nickel and Ammonium 384
Niccolo-nitrate of Ammonia.—$NH^3,NiO + NH^4O,NO^5$ 384

Page

Nickel and Potassium.

Niccolate of Potash 384
Sulphate of Nickel-oxide and Potash 384
Fluoride of Nickel and Potassium 385

Nickel and Sodium.

Niccolate of Soda 385
Nickel-oxide with Fluxes 385
¶ Metaphosphate of Nickel-oxide and Soda 385

Nickel, Barium, and Strontium.

Niccolate of Baryta and Niccolate of Strontia 386

Nickel and Calcium.

Niccolate of Lime 386

Nickel and Magnesium.

Niccolate of Magnesia 386
Phosphate of Nickel-oxide and Magnesia 386

Nickel and Aluminum.

Aluminate of Nickel-oxide 386
Fluoride of Aluminum and Nickel 386

Nickel and Silicium.

Hydrated Fluoride of Silicium and Nickel.—NiF,SiF^3+7Aq. 386
Glass-fluxes containing Nickel 386

Nickel and Tungsten.

Tungstate of Nickel-oxide.... 386
a. Monotungstate.—*b.* Bitungstate 386
Sulphotungstate of Nickel.—NiS,WS^3.... 387

Nickel and Molybdenum.

Molybdate of Nickel-oxide 387
Sulphomolybdate of Nickel.—NiS,MoS^3 387
Persulphomolybdate of Nickel.—NiS,MoS^4 387

Nickel and Vanadium.

Vanadiate of Nickel-oxide.
a. Monovanadiate.—*b.* Acid Vanadiate 387

Nickel and Chromium.

Chromate of Nickel-oxide.
a. Monochromate.—*b.* Acid Chromate 387

Nickel and Arsenic.

Arsenide of Nickel.
a. With very little Arsenic 388
b. With 4 At. Arsenic : *Placodine* 388
c. Trisarsenide : *Cobalt-speiss* 388

Page

d. Diarsenide: *Copper-nickel* 389
e. Mono-arsenide: *White Nickel-pyrites* 389
Arsenite of Nickel-oxide 390
Arseniate of Nickel-oxide: *Nickel-ochre* 390
Bisulphide of Nickel with Proto-arsenide of Nickel: *Nickel-glance* 391
Sulpharsenite of Nickel.—$2NiS,AsS^3$ 392
Sulpharseniate of Nickel.—$3NiS,AsS^5$, and $2NiS,AsS^5$ 392

Nickel and Antimony.

Antimonide of Nickel: *Antimonial Nickel* 392
Antimoniate of Nickel-oxide 393
Bisulphide of Nickel with Antimonide of Nickel: *Nickeliferous grey Antimony, Hartmannite* 393
Sulphantimoniate of Nickel.—$3NiS,SbS^5$ 393

Nickel and Tellurium.

Tellurite of Nickel-oxide 393
Tellurate of Nickel-oxide 393
Sulphotellurate of Nickel 393

Nickel and Bismuth.

Alloy of Nickel and Bismuth 393
Sulphide of Bismuth and Nickel: *Nickel-bismuth-glance* 393

Nickel and Zinc.

Alloy of Nickel and Zinc 394
Sulphate of Nickel-oxide and Zinc-oxide 394

Nickel and Tin.

Alloy of Nickel and Tin 394

Nickel and Lead.

Alloy of Nickel and Lead 394
Plumbite of Nickel-oxide 394

Nickel and Iron.

Alloys of Nickel and Iron 394
Meteoric Iron 395
Niccolate of Ferrous Oxide, and Ferrite of Nickel-oxide 396
Carbide of Nickel and Iron 396
Sulphide of Nickel and Iron: *Iron-nickel Pyrites* 396
Sulphate of Nickel-oxide and Ferrous Oxide 397

Nickel and Cobalt.

Alloy of Nickel and Cobalt 397

Other Compounds of Nickel 397

CHA 396
Memoirs, &c.—History.—Sources. 400
Preparation 402
Properties 403
COMPOUNDS OF COPPER. 405
Copper and Oxgyen 405
Cuprous Oxide.—Cu^2O 406
Hydrate of Cuprous Oxide 407
Cuprous Salts 408
Cupric Oxide.—CuO 413
Hydrate of Cupric Oxide 413
Cupric Salts 413
Peroxide of Copper? 413
¶ Cupric Acid? 414
Copper and Hydrogen. 414
Hydride of Copper? 414
Copper and Carbon. 414
Carbide of Copper 414
Carbonate of Cupric Oxide. 415
a. Dicarbonate. 415
α. Anhydrous: *Mysoline* 415
β. Hydrated: *Malachite* 415
b. Sesquicarbonate 415
c. Acid Carbonate 415
Copper and Boron. 415
Borate of Cupric Oxide 416
Copper and Phosphorus. 417
Phosphide of Copper.—a. Cu^6P 417
b. Triphosphide 417
c. Diphosphide 418
Hypophosphite of Cupric Oxide 418
Phosphite of Cupric Oxide 419
Phosphate of Cupric Oxide. 419
a. Sexbasic 41
b. Quintobasic: *Phosphorocalcite* or *Pseudo-malachite* 41
c. Quadrobasic: *Liebethenite* 4
d. Terbasic 4
e. Bibasic: *Trombolite* 4
f. Acid Phosphate 4
Pyrophosphate of Cupric Oxide 4
... of Cupric Oxide ....

Page

Copper and Sulphur.

Disulphide of Copper: *Copper-glance* 422
Protosulphide of Copper: *Indigo Copper, Blue Copper*, or *Breithauptite* 422
Pentasulphide of Copper 422
Hyposulphite of Cuprous Oxide 423
Sulphite of Cuprous Oxide 423
Sulphite of Cupric Oxide 424
Hyposulphate of Cupric Oxide.
a. Quadrobasic 424
b. Monobasic 425
Sulphate of Cupric Oxide.
a. Octobasic.—*b.* Quadrobasic: *Brochantite* 425
c. Bibasic ? 426
d. Monobasic: *Sulphate of Copper, Blue Vitriol* 427
a. Mono-hydrated.—β. Bi-hydrated.—γ. Penta-hydrated 430
Carbosulphide of Copper ? 430
Sulphocarbonate of Copper 431
Cuprous Hyposulphophosphite.
a. Bibasic: $2Cu^2S,PS$.—*b.* Monobasic: Cu^2S,PS 431
Cupric Hyposulphophosphite.—CuS,PS 431
Cuprous Sulphophosphite.—$2Cu^2S,PS^3$ 431
Cupric Sulphophosphate.
a. Octobasic: $8CuS,PS^5$.—*b.* Bibasic: $2CuS,PS^5$ 432

Copper and Selenium.

Diselenide of Copper, *or* Cuprous Selenide 432
Protoselenide of Copper, *or* Cupric Selenide 432
Selenite of Cuprous Oxide.... 432
Selenite of Cupric Oxide.
a. Basic.—*b.* Monoselenite 433
Seleniate of Cupric Oxide 433

Copper and Iodine.

Diniodide of Copper, *or* Cuprous Iodide 433
Iodate of Cupric Oxide 434
Periodate of Cupric Oxide.... 434

Copper and Bromine.

Dibromide of Copper, *or* Cuprous Bromide 435
Hydrobromate of Cuprous Oxide 436
Hydrobromate of Cuproso-cupric Oxide 436
Protobromide of Copper, *or* Cupric Bromide 436
Hydrobromate of Cupric Oxide 436
Cupric Oxybromide, *and* Basic Hydrobromate of Cupric Oxide 436
Bromate of Cupric Oxide.—*a.* Sexbasic 437
b. Monobasic 438

Page

Copper and Chlorine.

Dichloride of Copper, *or* Cuprous Chloride 438
Acid Hydrochlorate of Cuprous Oxide.... 439
Cupric Oxide with Cuprous Chloride.—$Cu^2Cl,2CuO$ 438
Aqueous Cuproso-cupric Chloride, *or* Hydrochlorate of Cuproso-cupric Oxide.... 438
Protochloride of Copper, *or* Cupric Chloride 438
Hydrated Protochloride of Copper, *or* Mono-hydrochlorate of Cupric Oxide 439
Cupric Oxychloride.
a. $CuCl,2CuO$ 440
b. $CuCl,3CuO$.—Hydrated: *Atakamite* 441
c. $CuCl,4CuO$ 442
Hypochlorite of Cupric Oxide 442
Chlorate of Cupric Oxide 442
Perchlorate of Cupric Oxide 442

Copper and Fluorine.

Difluoride of Copper, *or* Cuprous Fluoride 442
Protofluoride of Copper, *and* Monobasic Hydrofluate of Cupric Oxide 443
Hydrated Cupric Oxyfluoride, *or* Bibasic Hydrofluate of Cupric Oxide 443
Borofluoride of Copper.—CuF,BF^3 443

Copper and Nitrogen.

Nitride of Copper.
a. With very great excess of Copper 444
b. Somewhat richer in Nitrogen ?.... 444
c. Cu^6N 444
Nitrite of Cupric Oxide 446
Nitrate of Cupric Oxide.
a. Terbasic.—*b.* Monobasic 446
Cuprous Oxide with Ammonia 447
Cupric Oxide with Ammonia 447
Carbonate of Cupric Oxide with Ammonia 448
Boride of Nitrogen and Copper ? 448
Cupro-hyposulphate of Ammonia 448
Ammonio-sulphate of Cupric Oxide.—$5NH^3+2(CuO,SO^3)$ 448
Cupro-sulphate of Ammonia.—$NH^3,CuO+2NH^4O,SO^3$ 449
Bibasic-sulphate of Cupric Oxide and Ammonia.—NH^3,CuO,SO^3 450
Sesquibasic Sulphate of Cupric Oxide and Ammonia.—$NH^3,2CuO,2SO^3$.... 450
Monobasic Sulphate of Cupric Oxide and Ammonia.—$NH^4O,SO^3+CuO,SO^3+6Aq.$ 450
Ammonio-diniodide of Copper.—$2NH^3,Cu^2I$ 450
Ammonio-protiodide of Copper.—$2NH^3,CuI+Aq.$.... 451
Cupro-iodate of Ammonia 452
Ammonio-dibromide of Copper 452

Page

Ammonio-protobromide of Copper.
a. $5NH^3,2CuBr$.—*b.* $3NH^3,2CuBr$ 452
Cupro-bromate of Ammonia.—$NH^3,CuO+NH^3,BrO^5$ 452
Ammonio-dichloride of Copper 453
Dichloride of Copper and Ammonium: *Cuproso-ammonic Chloride* 453
Ammonio-protochloride of Copper.
a. With 3 At. Ammonia.—$3NH^3,CuCl$ 453
b. With 2 At. Ammonia.—$2NH^3,CuCl+HO$ *or* $NH^3,CuO+NH^3,HCl$ 453
c. With 1 At. Ammonia.—$NH^3,CuCl$ 454
Protochloride of Copper and Ammonium: *Cuprico-ammonic Chloride.*
a. $NH^4Cl,CuCl+2Aq$. 454
¶ *b.* $NH^4Cl,2CuCl+4Aq$. 455
Cupro-nitrate of Ammonia.... 455
¶ Azophosphate of Cupric Oxide 456

Copper and Potassium.
Alloy of Copper and Potassium 456
Cuprous Oxide with Potash 456
Cupric Oxide with Potash 457
Carbonate of Cupric Oxide and Potash 458
Sulphide of Copper and Potassium 458
Hyposulphite of Cuprous Oxide and Potash.
a. $KO,S^2O^2+Cu^2O,S^2O^2+2Aq$. 458
b. $3(KO,S^2O^2)+Cu^2O,S^2O^2+3Aq$. 459
Sulphite of Cuprous Oxide and Potash 459
Sulphate of Cupric Oxide and Potash 459
Seleniate of Cupric Oxide and Potash 460
Diniodide of Copper and Potassium: *Cuproso-potassic Iodide* 460
Dichloride of Copper and Potassium: *Cuproso-potassic Chloride* 460
Protochloride of Copper and Potassium: *Cuprico-potassic Chloride* 460
Fluoride of Copper and Potassium 461

Copper and Sodium.
Cupric Oxide with Soda 461
Carbonate of Cupric Oxide and Soda 461
Copper with Fluxes 461
Hyposulphite of Cuprous Oxide and Soda.
a. $2(NaO,S^2O^2)+3(Cu^2O,S^2O^2)+5Aq$. 461
b. $3(NaO,S^2O^2)+Cu^2O,S^2O^2+2Aq$. 462
Sulphate of Cupric Oxide and Soda 462
Dichloride of Copper and Sodium: *Cuproso-sodic Chloride* 462

Copper and Barium.
Alloy of Copper and Barium ? 462

Page

Cupric Oxide with Baryta ? 463
Sulphide of Copper and Barium 463
Dichloride of Copper and Barium: *Cuproso-barytic Chloride* 463

Copper and Calcium.
Cupric Oxide with Lime 463
Sulphide of Copper and Calcium 463
Cupric Sulphate with Fluoride of Calcium 463

Copper and Magnesium.
Sulphide of Copper and Magnesium 463
Sulphate of Cupric Oxide and Magnesia 463
Sulphate of Cupric Oxide, Magnesia, and Ammonia 463

Copper and Aluminum.
Aluminate of Cupric Oxide 464
Fluoride of Aluminum and Copper 464

Copper and Zirconium.
Zirconate of Cupric Oxide 464

Copper and Silicium.
Silicide of Copper 464
Silicate of Cupric Oxide.
a. Monosilicate.
α. Mono-hydrated: *Emerald-copper* or *Dioptase* 464
β. Bi-hydrated: *Chrysocolla*.... 465
b. Quadrosilicate.... 465
Cuprous Silicofluoride.—Cu^2F,SiF^2 465
Cupric Silicofluoride.—$CuF,SiF^2+7Aq.$ 465
Cuprous Oxide with Glass-fluxes 466

Copper and Titanium.
Hydrated Fluoride of Titanium and Copper 466

Copper and Tungsten.
Alloy of Copper and Tungsten 466
Tungstate of Cupric Oxide.
a. Monotungstate.—*b.* Bitungstate 466
Sulphotungstate of Copper.—CuS,WS^3 466

Copper and Molybdenum.
Alloy of Copper and Molybdenum 467
Molybdate of Cupric Oxide 467
Sulphomolybdate of Copper.—CuS,MoS^3 467
Persulphomolybdate of Copper.—CuS,MOS^4 467

Copper and Vanadium.
Vanadiate of Cupric Oxide.
a. Monovanadiate.—*b.* Bivanadiate 467

Copper and Chromium.
Chromate of Cupric Oxide.
a. Polybasic ? 467
b. Basic ?—*c.* Monochromate 468

Page

Chromate of Cupric Oxide and Ammonia 468

Copper and Uranium.

Phosphate of Uranic Oxide and Cupric Oxide: *Chalkolite* 468

Copper and Manganese.

Alloy of Copper and Manganese 468

Peroxide of Manganese with Cupric Oxide: *Cupreous Manganese* 468

Permanganate of Cupric Oxide 468

Copper and Arsenic.

Arsenide of Copper.

a. Containing but a small quantity of Copper 470

b. Cu^4P.—*c.* Cu^3P 470

Arsenite of Cupric Oxide.

a. Mono-arsenite? *Scheele's Green* 470

b. Acid Arsenite 470

Arseniate of Cupric Oxide.

a. Octobasic? *Copper-mica* 471

b. Pentabasic.

α. Bi-hydrated: *Erinite* 471

β. Penta-hydrated: *Aphanese* 471

γ. Deca-hydrated: *Leirochroite* 472

c. Quadrobasic.

α. Mono-hydrated: *Olivenite*.... 472

β. Hepta-hydrated: *Euchroite* 473

γ. Deca-hydrated: *Lirocconite* 473

d. Terbasic 473

Cupric Sulpharsenite.

a. $12CuS,AsS^3$.—*b.* $3CuS,AsS^3$ 474

c. $2CuS,AsS^3$ 474

Cupric Sulpharseniate.—$2CuS,AsS^5$ 474

Copper and Antimony.

Antimonide of Copper 474

Antimonic Oxide with Cuprous Oxide.... 474

Antimonite of Cupric Oxide 475

Antimoniate of Cupric Oxide 475

Cuprous Sulphantimonite: *Antimonial Copper-glance.*—Cu^2S,SbS^3 476

Cupric Sulphantimoniate.—$3CuS,SbS^5$.... 476

Antimonide of Copper and Potassium 476

Copper and Tellurium.

Telluride of Copper 477

Tellurite of Cupric Oxide 477

Tellurate of Cupric Oxide 477

Sulphotellurite of Copper.—$3CuS,TeS^2$ 477

Copper and Bismuth.

Alloy of Bismuth and Copper 477

Sulphide of Bismuth and Copper: *Copper-bismuth-glance* 477

Page

Copper and Zinc.

Alloys of Copper and Zinc 477
a. Tombac, Pinchbeck, &c. 479
b. Brass.—*c.* Mosaic Gold.—*d.* Brazier's Solder 480
Carbonate of Cupric Oxide and Zinc-oxide: *Aurichalcite* 480
Sulphate of Cupric Oxide, Zinc-oxide, and Potash 481

Copper and Cadmium.

Alloy of Copper and Cadmium 481

Copper and Tin.

Alloys of Copper and Tin: *Bronze, Gun-metal, Bell-metal,* &c. 481
Stannate of Cuprous Oxide 483
Stannate of Cupric Oxide 484

Copper and Lead.

Alloy of Copper and Lead 484
Cuprous Oxide with Lead-oxide 484
Cupric Oxide with Lead-oxide 485
Sulphide of Copper and Lead 485
Hyposulphite of Cupric Oxide and Lead-oxide? 485
Selenide of Copper and Lead.
a. 4PbSe,CuSe 485
b. 2PbSe,CuSe: *Selenkupferblei* 485
c. PbSe,CuSe: *Selenbleikupfer* 486
Chromate of Cupric Oxide and Lead-oxide: *Vauquelinite* 486
Antimonide of Copper and Lead 487
Sulphide of Antimony, Copper, and Lead.
a. Bournonite 487
b. Prismatoidal Copper-glance 488
Sulphide of Bismuth, Copper, and Lead: *Needle-ore* 488
Alloy of Copper, Lead, Tin, and Zinc 488

Copper and Iron.

Alloy of Copper and Iron 489
Carbide of Copper and Iron 489
Sulphide of Copper and Iron.
a. Purple Copper, Phillipsine.... 489
b. Copper-pyrites 491
Sulphate of Cupric Oxide and Ferrous Oxide: *Ferroso-cupric Sulphate* 492
Sulphantimoniate of Copper and Iron: *Fahl-ore* or *Grey Copper* 492
a. Tennantite 492
β. Light grey Copper.—γ. Dark grey Copper 493
δ. Silver Fahl-ore.—ε. Quicksilver Fahl-ore 494
Alloy of Copper, Iron, and Zinc 496
Sulphostannate of Iron and Copper: *Tin-pyrites* 496

Page

Copper and Cobalt.

Sulphate of Cupric Oxide and Cobalt-oxide: *Cobaltoso-cupric Sulphate* 496

Copper and Nickel.

Alloy of Nickel and Copper 497
Sulphate of Cupric Oxide and Nickel-oxide 497
Sulphate of Cupric Oxide, Nickel-oxide, and Potash 497
Alloy of Copper, Nickel, and Zinc: *Nickel-silver, German Silver, White Copper, Packfong* 497

Other Compounds of Copper 499

Su

a. T.

β. Lig.

δ. Silv.

Alloy of Cop.

Sulphostannat.

METALS,

(*Continued.*)

CHAPTER XXVIII.

ZINC.

Bergman. De mineris Zinci. *Opusc.* 2, 209.
De Lassonne. *Crell. Chem. Journ.* 3, 165, and 5, 59.
A. Vogel. *Schw.* 11, 408.
Schindler. *Mag. Pharm.* 31, 167; 36, 43.
Wackenroder. *Ann. Pharm.* 10, 63; 11, 151; 42, 348.—*N. Br. Arch.* 16, 133.
Kane. *Ann. Chim. Phys.* 72, 290.

SYNONYMES. *Spelter, Spiauter, Zink, Zincum.*

History. The ore of zinc called *Calamine,* or *Cadmia,*—but not the pure metal—was known to the ancient Greeks and used in the manufacture of brass. The metal zinc was first mentioned by Paracelsus; it was for a long time imported from the East, but since the middle of the eighteenth century, it has been prepared in Europe.

Sources. As oxide; as carbonate; as sulphide; as sulphate; as aluminate; as silicate; as a compound of ferric oxide with zinc-oxide; and as a double carbonate of copper and zinc.

Preparation. Native carbonate or silicate of zinc-oxide, freed by previous roasting from carbonic acid and water—or zinc-oxide obtained by prolonged roasting from the native sulphide—or zinc-oxide which has sublimed in the upper part of the furnace-shaft during the fusion of other ores, is mixed with about $\frac{1}{3}$ of its weight of charcoal-powder, and heated to a low white heat in retorts or retort-like vessels of earthenware or iron: the zinc is then reduced and volatilized, and condenses in the colder part of the apparatus. In Silesia, the mixture of zinc-oxide and charcoal or coke is heated in muffles 3 feet long and $1\frac{1}{2}$ foot high, six of which (three side by side) are laid in one furnace. The evolved mixture of carbonic oxide gas and zinc vapour passes from the upper and fore part of the muffles, through a knee-shaped channel, horizontal in the nearer and directed downwards in the farther part, and the zinc condenses

therein and drops down from its lower aperture. Part of the zinc vapour, and likewise some cadmium vapour, escapes uncondensed together with the carbonic oxide gas, and burns in the air, producing the substance called *Silesian Zinc-flowers.* (*Schlesische Zinkblumen.*) In Liège, the reduction is performed in earthenware tubes, laid side by side. The zinc, as it condenses in the fore part of these tubes, is scraped out from time to time in the liquid state. In England, a number of cast-iron pots are arranged in a circle in one common furnace. Through the bottom of each of these pots there passes a tube open at both ends. The vessels are filled with the mixture to such a height as not to stop up the upper end of the tube, then closed with a well-fitting cover, and heated. The zinc drops down from the part of the tube which descends from the bottom of the crucible. This process is called *Destillatio per descensum.*— 2. At Goslar, zinc is obtained as a secondary product in the smelting of lead ores. The zinc vapours condense in the upper half of the furnace, and run down from the shaft upon a slanting stone called the *zinc-stool.* (*Zinkstuhl.*) The zinc thus obtained is melted in iron pots and poured out on tables.

Commercial zinc may contain charcoal, sulphur, manganese, arsenic, antimony, cadmium, tin, lead, iron, cobalt, nickel, and copper. Uranium has likewise been mentioned as an impurity in zinc, but probably copper was mistaken for it. Carbon is contained in zinc in the form of charcoal splinters, according to Wackenroder, and as carbide of zinc, according to Gren, Berzelius, and Schindler. East Indian zinc contains only 0·43 per cent. of lead and 0·24 of iron. (Bonnet.) Silesian zinc contains a large quantity of cadmium, besides charcoal, lead, iron, and a very small quantity of copper. (Wackenroder, Jansen.) Houton-Labillardière and G. Barruel (*Compt. rend.* 14, 724; also *J. pr. Chem.* 26, 383) found tin in several sorts of zinc. Three samples of East Indian zinc were found by Wittstein (*Report.* 55, 193) to give the results *a*, *b*, *c*; *d* is an analysis by Jacquelain (*Compt. rend.* 14, 636; also *J. pr. Chem.* 26, 298) of a sample of unknown origin.

	a.	*b.*	*c.*	*d.*
Zn	96·27	99·05	98·76	99·170
Pb	3·33	0·27	0·91	0·685
Cd	0·30	0·23	0·16	
Fe	0·10	trace	0·17	0·142
C				0·003
	100·00	99·55	100·00	100·000

Commercial zinc, when dissolved in dilute sulphuric acid, leaves a black powder. In Silesian zinc, this residue amounts to 2 per cent., and consists of sulphide of lead and charcoal splinters. (Wackenroder.) A. Vogel found in this black powder, carbon, sulphur, lead, and iron; Jacquelain found carbon, lead, and iron: he likewise obtained the same residue, but containing less lead, by distilling zinc in a stream of hydrogen. G. Barruel, by reducing in a charcoal crucible the powder which remained after dissolving zinc in dilute sulphuric acid, obtained an alloy containing 58·6 p.c. tin, 34·5 lead, 5·5 sulphur, with traces of iron and manganese.

Purification. 1. The zinc is distilled once or twice either in an earthen retort (the neck of which, however, is soon stopped up by the sublimed zinc), or else in an earthen or iron crucible, into the bottom of

which is luted a tube open at both ends and reaching nearly to the top; the mouth of the crucible is stopped with a well-fitting cover.—Wittstein (*Repert.* 61, 220) introduces into an uncoated Hessian retort, capable of holding from 24 to 30 ounces of water, 4 pounds of comminuted zinc, heats it gradually in a wind-furnace covered with a dome six feet high—and, when the distillation has begun, which takes place after an hour or an hour and a half, and the zinc condenses in the neck of the retort, scrapes it out with a curved iron wire, while still liquid, into a basin containing water and placed below to receive it. If the scraping be not assiduously kept up, the neck becomes stopped up with solid zinc; if the neck is too short, some of the zinc burns away. This process yields about 3¼ pounds of zinc, still containing cadmium; a greenish yellow powder remains in the retort.—Jacquelain (*N. Ann. Chim. Phys.* 7, 199) distils the zinc in a current of hydrogen. The hydrogen is evolved in a Woulfe's bottle from purified sulphuric acid, zinc, and water, and made to pass, first through solution of potash, then through two chloride of calcium tubes, then into a red-hot porcelain tube, in which are placed little boats or dishes of porcelain containing the zinc to be purified, and lastly through a knee-shaped tube into oil of vitriol. The zinc is deposited in the colder part of the porcelain tube (antimony and cadmium may be distilled in a similar manner).—Distillation, however, does not purify the zinc completely, especially from the more volatile metals, such as cadmium and lead; according to Berzelius and Dulong (*Ann. Chim. Phys.* 15, 388), the zinc after distillation contains the same impurities as before.

2. Sulphur, either alone or mixed with grease, is repeatedly stirred about with a stick at the bottom of melted zinc, in order to convert the foreign metals into sulphides. The more briskly the sulphur is stirred about, the more complete is the purification: the process, however, does not remove the whole of the lead and iron. (Bonnet, Schwake, *Ann. Pharm.* 9, 184.)

3. Commercial zinc fused and very hot is poured into a deep bucket filled with water, in order to granulate it as finely as possible; 1 part of this granulated zinc is then placed, together with ¼ pt. nitre, in a crucible, in such a manner that there may be a small portion of free nitre both at top and bottom, and the whole is heated in the furnace till vivid combustion ensues. The crucible is then taken out, the slag removed, and the zinc poured out. The zinc thus treated is free from arsenic and iron. (Maillet, *J. Pharm.* 27, 625.)

4. To obtain perfectly pure zinc, it is necessary to distil perfectly pure zinc-oxide with lamp-black (or charcoal) in a retort, and free the product from any charcoal that may be mixed with it, by a second distillation: but this distillation, on the small scale, is attended with many difficulties.

Testing. The hydrogen gas evolved on dissolving the zinc in pure dilute sulphuric acid should give no precipitate when passed through solutions of lead, silver, or gold salts; a precipitate would indicate the presence of sulphur or arsenic; it must neither yield arsenic spots, nor deposit metallic arsenic when passed through a red-hot tube (IV. 268); fuming nitric acid through which the gas has been passed ought to evaporate completely over the water-bath: sulphur, arsenic, or antimony would remain behind in the form of an acid.—The zinc when dissolved in dilute sulphuric acid must leave no residue. The resulting solution of

zinc-sulphate, when supersaturated with sulphuric acid, must give no precipitate with sulphuretted hydrogen (cadmium, copper, tin); metallic zinc immersed in it should produce no metallic deposit (cadmium, tin, copper). The precipitate which potash produces in the solution of the sulphate should be perfectly soluble in excess of the re-agent (the oxides of iron, copper, and cadmium would be left undissolved). The solution of the zinc in aqua-regia should give no precipitate with chloride of barium,—that is to say, it must be free from sulphuric acid.

Properties. Crystallizes in long, regular, six-sided prisms. (Nöggerath, *Pogg.* 39, 324.) According to former statements, it crystallizes in four-sided prisms and needles. Zinc containing from 3 to 4 per cent. of iron was found by Laurent and Holms (*Ann. Chim. Phys.* 60, 333) in the cracks of the earthen tubes in which it had been distilled, crystallized in rhombic prisms. ¶. Nicklès (*N. Ann. Chim. Phys.* 22, 37) states that zinc prepared by Jacquelain's method of distillation in a current of hydrogen, crystallizes in well-defined pentagonal dodecahedrons: hence it is dimorphous. ¶. Zinc has a broadly laminar texture. It is moderately hard, difficult to file, and when bent after fusion, emits a crackling noise, but not so loud as tin. If hammered with great violence, it splits in the direction of the cleavage-planes; but by careful pressure, whereby it loses its crystalline structure, it may be rendered ductile, and may then be extended into thin plates or wires. According to Hobson and Sylvester (*Gilb.* 24, 104), it exhibits its greatest degree of ductility and malleability at temperatures between 100° and 150°; at 205°, on the contrary, it is so brittle that it may be pounded in a mortar. Hence, to obtain zinc-plate, or zinc-foil, the metal cast in a tabular form is heated in a boiling solution of common salt, and then passed between rollers. To obtain pulverized zinc, on the other hand, the melted metal is poured into a strongly heated crucible, and the heated mass strongly rubbed and stirred with an iron pestle till it solidifies. (Böttger, *Ann. Pharm.* 34, 85.)—The specific gravity of commercial zinc solidified after fusion is 6·861 (Brisson); of purified zinc, 6·9154 (Karsten); of rolled commercial zinc, 7·1908 (Brisson). Zinc has a bluish grey-white colour, and a strong lustre. Fuses at 260° (Black), at 374° (Morveau), at 412° (Daniell), and boils at a white heat. Contracts strongly in solidifying from fusion (Marx).

Atomic Weight. 32·26, Berzelius; 33·09, Jacquelain; 33, Favre (*Ann. Pharm.* 48, 193).

Compounds of Zinc.

Zinc and Oxygen.

A. *Sub-oxide of Zinc?*

Zinc exposed to the air at ordinary temperatures, becomes covered with a thin grey film, which prevents the further oxidation of the inner portions. Zinc heated just to the melting point, oxidates still more rapidly, and forms a grey powder, which, however, is soon converted into the white oxide. Berzelius regards this grey substance as a sub-oxide; Proust, Davy, and A. Vogel regard it as a mixture of the metal and the oxide.

B. Zinc-oxide. ZnO.

Oxide of zinc, Protoxide of zinc, Zinkoxyd, Oxyde zincique.—Red zinc-ore is a mixture of 88 parts zinc-oxide and 12 parts manganoso-manganic oxide.

Formation. Zinc heated to redness in the air burns with a dazzling bluish and greenish flame, and forms zinc-oxide, which partly remains in the crucible, partly rises up in the air, and falls down again in large flakes—*Flowers of zinc, Zinkblumen, Flores zinci, Lana philosophica, Nihilum album.* When it has once taken fire, it continues to burn, even after the crucible has been removed from the furnace, till the whole is converted into oxide, provided it be constantly stirred and the oxide removed as it forms. (Sementini.) Zinc heated in the air just to the melting point, is gradually converted, first into sub-oxide and then into oxide.—2. At ordinary temperatures, zinc remains bright in dry air. If water be present, the hydrated oxide is formed; and if the air likewise contains carbonic acid, hydrated basic carbonate of zinc is produced. Zinc placed under a receiver surrounded at the bottom with water and containing air free from carbonic acid, becomes covered with drops of moisture, and tarnished on the surface by the formation of a whitish-grey film of hydrated oxide. But if a piece of tarnished lead be placed under the same receiver, though not in contact with the zinc, the drops of water are deposited only on the lead, not on the zinc, which therefore remains bright. Under water which is in contact with air free from carbonic acid, zinc becomes covered with hydrated oxide containing 7 per cent. of water. Zinc exposed to moist air containing carbonic acid,—to the open air, for example,—becomes covered with hydrated basic carbonate of zinc. The same salt is formed when zinc is exposed to the air under water. (Von Bonsdorff, *Pogg.* 42, 325.) When zinc is exposed to the air, under water containing $\frac{1}{300}$ of hydrate of potash, it turns grey, and forms white shining laminæ of carbonate of zinc: no zinc is dissolved in the water. (A. Vogel, *J. pr. Chem.* 14, 107.)—The following remarkable observations of Bonsdorff may likewise be added in this place. Whenever two metals are placed—not in contact with each other—under a bell-jar containing air and closed at the bottom with water, only the more oxidable metal is bedewed, and therefore oxidated: *e.g.* arsenic or lead placed in a moist atmosphere near copper or silver. Copper or silver placed alone under the bell-jar condenses the dew on its surface. The contrary effect takes place if the metals are in contact: thus, when copper is in contact with zinc, the copper alone is bedewed; when copper is in contact with silver, the condensation of moisture takes place only on the silver.—Zinc does not decompose pure water at ordinary temperatures; but at a red heat or in presence of acids or alkalis, the decomposition takes place. Zinc sealed up in a glass tube together with water deprived of air by boiling, remains bright for years. (Bonsdorff, Boutigny, *Ann. de Hyg. publ.* 17, 290.) It does not decompose pure water, even on boiling; and even when placed in contact with copper, it does not decompose pure water, but only water containing a salt. (J. Davy, *N. Ed. Phil. J.* 17, 47.) When vapour of water is passed over zinc at a low red heat, hydrogen gas is set free, and small crystals of zinc-oxide are deposited upon the metal: if the zinc is strongly ignited, the oxide sublimes on the tube in small shining crystals. (Regnault, *Ann. Chim. Phys.* 62, 350.) If the zinc is

[illegible] the oxide is obtained partly in amorphous globules, partly [illegible] (Hadat, [illegible] 46, 72.) All [illegible] oxygen somewhat strongly—even weak acids—[illegible] water and zinc. The purer the zinc, the more [illegible] dilute acids, unless it is in contact with platinum [illegible] metal I. 347.) In aqueous alkalis, solu- [illegible] than in acids.—4. Red-hot zinc converts [illegible] oxide, and forms with phosphoric acid a [illegible] and phosphate of zinc-oxide. In the moist [illegible] strong sulphuric acid (on the appli- [illegible] molybdic, and arsenic acid. From [illegible] barium, bismuth, cadmium, tin, lead, [illegible] silver, gold, platinum, palladium, [illegible] dissolved in acids, it withdraws all the [illegible] being itself dissolved in the form of [illegible] of titanium, tungsten, molybdenum, [illegible] manganese, and iron, dissolved or diffused [illegible] oxygen.

[illegible] easily to combustion in a capacious [illegible] position—the surface of the [illegible] oxide, which is deposited in woolly [illegible] the crucible, and then rubbed up in [illegible] glittering grains of metallic zinc. [illegible] which, if they are prepared from [illegible] of the metals with which the [illegible] Wistein recommends zinc purified [illegible] any other soluble zinc-salt) is [illegible] mixed with an alkaline carbonate [illegible] the latter thoroughly washed, [illegible] process gives the zinc-oxide [illegible] *vitriolum humida paratum.*— [illegible] The white vitriol of commerce [illegible] usually contains sulphate of [illegible] that obtained by dissolving [illegible] oil of vitriol often contains [illegible] alumina, it is best to use the [illegible]—arsenic, cadmium, tin, lead [illegible] sulphate of lead is nearly inso- [illegible] and cobalt. The quantity of [illegible] sulphuretted, when the dilute acid [illegible] Precipitating the solution of zinc- [illegible] that a portion of the [illegible] water and longer gives a white [illegible] with sulphuretted [illegible] several days, the [illegible] precipitated in the [illegible] and filtered without [illegible] dissolve— [illegible] If the [illegible] works in an open [illegible] more gas [illegible] precipitable by [illegible] state by the

excess of zinc; so that the solution, when acidulated with sulphuric acid, gives no precipitate with sulphuretted hydrogen, and consequently the treatment with that liquid may be dispensed with. The cadmium, tin, lead, and copper may likewise be precipitated in the metallic state by leaving the solution of the zinc-sulphate for some time, either warm or cold, in contact with metallic zinc, or by boiling it with that metal (Dalk, *Berl. Jahrb*, 24, 2, 74; Horst, *Br. Arch.* 7, 75; Wackenroder): in all cases, however, a portion of the solution thus purified should be mixed with excess of sulphuric acid, then saturated with sulphuretted hydrogen, and left to itself for a few days. If a precipitate is thereby produced, the whole of the solution must be treated with sulphuretted hydrogen.

It still remains to separate any iron, cobalt, nickel, or manganese that may be present. If the object in view is the preparation of pure zinc-sulphate, the solution is first freed from a portion of the metals just mentioned, and likewise from the excess of acid, by evaporating and cooling, and then decanting the mother-liquid from the crystals. The crystals are then re-dissolved in water; $\frac{1}{10}$ of the solution mixed with carbonate of soda to precipitate carbonate of zinc; the precipitate, after thorough washing, diffused through the rest of the solution; and chlorine gas passed through the liquid, which must be constantly agitated, till a large portion of the zinc-carbonate is dissolved, and the rest has acquired a brownish colour from admixture of sesquioxide of iron and the peroxides of manganese, cobalt, and nickel. The liquid is then set aside for some time in a warm place and frequently agitated—afterwards mixed with sulphuric acid, because a basic salt has been formed in the preceding process; then evaporated to the crystallizing point, and the crystals freed by re-crystallization from adhering chloride of zinc. The same end may be attained by the following methods:—Veltmann (*Berl. Jahrb.* 29, 1, 59) mixes the solution of zinc-sulphate with chlorine-water (which, however, requires the use of large vessels), and adds zinc-oxide to it. Schindler (*Mag. Pharm.* 26, 74) saturates the dilute solution with chlorine (a concentrated solution does not absorb enough) and then digests it with zinc-oxide. Bonnet (*Inn. Pharm.* 9, 165) precipitates carbonate of zinc from a portion of the solution, washes it, diffuses it in water, passes chlorine gas through the liquid, and mixes the resulting oxychloride of zinc with the rest of the solution. If, on the other hand, the preparation of pure zinc-oxide from the solution be the only object in view, the liquid is mixed with a quantity of carbonate of soda sufficient to produce a copious precipitate; chlorine gas passed through it, with agitation, till the greater part of the precipitate is dissolved; and the solution filtered. (Grove, *Br. Arch.* 22, 40; Wackenroder.) Or, the solution of zinc-sulphate is mixed with chloride of soda, then left to itself for 24 hours, and carbonate of soda cautiously added till a perfectly white precipitate begins to form. (Jansen, *Mag. Pharm.* 26, 74; Herberger, *Repert.* 48, 382; Frederking, *Repert.* 56, 72.) The chloride of soda must be prepared with carbonate of soda and chlorine gas, not with carbonate of soda and chloride of lime, because in that case it might contain lime. Hermann (*Schw.* 46, 249) mixes the solution with chloride of lime containing excess of lime; evaporates the liquid to the crystallizing point; separates the crystals from the mother-liquid, which may still contain cobalt and nickel; dissolves them in the smallest possible quantity of cold water, and filters to separate gypsum. Zinc-oxide thus prepared may contain lime and magnesia, because the gypsum may not be completely

separated, and the lime used in preparing chloride of lime often contains magnesia. (Greve, Veltmann, Wackenroder.)

There are likewise a few methods of purification, chiefly directed towards the separation of iron. The solution mixed with carbonate of zinc is exposed to the air for several months till the iron is completely precipitated. (Martius, *Repert.* 41, 203; Clamor-Marquart, *Ann. Pharm.* 7, 20.) The solution is boiled with zinc-oxide. (Geiger.) Since the precipitation of the iron depends upon its conversion from protoxide into sesquioxide by the oxygen of the air, it would be necessary, in applying this method, to heat the solution for a long time, and in that case basic sulphate of zinc would be formed. (Wackenroder.) A solution of 16 parts of zinc-sulphate is boiled with 1 part of nitric acid, till it is reduced to a thickish mass; then re-dissolved in water, boiled with 1 or 1½ pt. pure zinc-oxide, and filtered. (Trommsdorff, *Taschenb.* 1823, 1.) It is not easy to oxidize the iron completely; the filtrate contains basic zinc-sulphate which must be re-converted into monosulphate by the addition of a small quantity of sulphuric acid. (Schindler.) 9 parts of crystallized zinc-sulphate are heated in a crucible with 1 part of nitre, gently at first —then, after the water of crystallization has been driven off, to strong redness—and kept at that heat till a portion dissolved in water yields a filtrate free from iron: the whole is then dissolved in water and filtered. (Bucholz, *Pharm. Boruss.*) Artus (*J. pr. Chem.* 26, 508) mixes 50 parts of finely powdered zinc-sulphate very intimately with 1 part of nitre; heats the mixture in a crucible, stirring it all the while with a porcelain spatula, till it is dry; then raises the heat somewhat higher; afterwards dissolves in hot water; filters to separate oxide of iron, and boils the filtrate for a short time with purified charcoal to separate any manganese that may be present. Geiger recommends igniting the zinc-vitriol with $\frac{1}{10}$ nitrate of zinc-oxide or baryta; if the latter salt be used, strong ignition is necessary. Dalk mixes the solution of zinc-sulphate with infusion of galls, and exposes it to the air in a basin as long as a violet film continues to form upon it; then evaporates to dryness, dissolves, and filters. To remove the excess of tannin, Wittstein (*Repert.* 65, 218) digests the filtrate for 24 hours with recently ignited charcoal; and Walcker (*Ann. Pharm.* 4, 84) precipitates it by boiling with white of egg. A solution of 4 parts zinc-sulphate in 20 water set aside for 5 days in contact with recently ignited wood-charcoal deposits all the iron it contains upon the charcoal. (Stickel, Wittstein.)

It has likewise been proposed to dissolve zinc in hydrochloric, nitric, or acetic acid, and then purify the solution in a similar manner.

¶ Defferre (*J. Pharm.* 5, 70) dissolves 125 parts of zinc in 500 parts of hydrochloric acid—then adds 8 parts of nitric acid, and warms the liquid to oxidize the iron; evaporates to dryness; dissolves the residue in water; leaves the solution for 24 hours in contact with 8 parts of carbonate of lime, and filters. The clear liquid is precipitated while hot, by gradually adding dilute ammonia as long as any precipitate continues to form, the solution retains but very little zinc-oxide, and the precipitate, after thorough washing, contains scarcely a trace of any other salt. ¶

b. Precipitation of the purified Zinc-solution.—The solution is boiled in a porcelain basin, and carbonate of soda added in small portions till slightly in excess; the boiling is then continued for a time, in order that the precipitate may aggregate more closely. Or, a dilute solution of 1 At. zinc-sulphate is precipitated, in the cold and with agitation, by a solution of somewhat less than 1 At. carbonate of soda, the filtering being

deferred for some time in order that the gelatinous precipitate may become pulverulent. Another method is to boil a solution of 9 parts of crystallized carbonate of soda in a clean copper vessel, and cause a solution of 2 parts of zinc to flow into it in a thin stream—the soda-solution being constantly stirred—so that the liquid may not boil over from escape of carbonic acid, nor the undecomposed zinc-solution come in contact with the copper vessel. The precipitate is easy to wash, and is free from soda, provided the boiling has been kept up during the whole time of mixing. (Schindler.) If any portions of soda and sulphuric acid are carried down with the precipitate, the greater part may be removed by boiling for a while after precipitation, but not all. (Wackenroder.) If the zinc-solution be precipitated by carbonate of soda in the cold, an excess of the latter must be avoided, as otherwise the precipitate will retain its gelatinous character even after long standing, and will contain considerable quantities of soda and sulphuric acid. For 1 part of zinc-vitriol dissolved in 20 parts of water, 1 part of crystallized carbonate of soda dissolved in 10 parts of water is sufficient. The two solutions are mixed at once, and rapidly stirred; the transparent jelly thereby produced is converted in the course of 24 or 36 hours, with evolution of gas, into a loose powder which is easy to wash. Acid carbonate of zinc remains in solution, together with any lime and magnesia that may perchance be present. The oxide obtained by ignition from the carbonate precipitated in the cold exhibits a fainter tinge of yellow than that prepared from carbonate precipitated from hot solutions. (Schindler, Wackenroder.) The zinc-solution may likewise be mixed in the cold with carbonate of ammonia, till the liquid is perfectly neutral. The precipitate, like that produced by cold carbonate of soda, contains but a trace of sulphuric acid. The precipitate obtained with carbonate of ammonia in a hot solution, contains a considerable quantity of sulphuric acid. (Wackenroder.) Precipitation by caustic ammonia, potash, or soda, does not give good results; if too small a quantity of the alkali be used, a basic salt is precipitated; with a larger quantity, the precipitate is liable to be contaminated with an alkaline salt, and a still larger quantity completely re-dissolves it. The precipitated zinc-carbonate is washed partly by subsidence and decantation, partly by pressure, and lastly on the filter. The dried precipitate is gently ignited in a covered earthen crucible.—The most direct mode of obtaining pure zinc-oxide would be to precipitate pure nitrate of zinc by carbonate of ammonia, and ignite the precipitate.

Testing of the Zinc-oxide.—The oxide prepared by (1) should be white; that obtained by (2) white, with a faint tinge of lemon-yellow. A brownish white tint indicates the presence of foreign metallic oxides; pure whiteness and considerable density in the oxide (2) shows the presence of sulphuric acid, chlorine, and soda.—1. *Metallic zinc:* Evolution of hydrogen on solution in acids.—2. *Sulphuric acid* or *chlorine:* The solution of the oxide in nitric acid gives a precipitate with chloride of barium or nitrate of silver.—3. *Soda:* May be extracted by water, partly in combination with sulphuric or hydrochloric acid.—4. *Lime* and *Magnesia:* The solution of the oxide in hydrochloric acid, when precipitated by hydrosulphate of ammonia and filtered, yields chloride of calcium or magnesia, on evaporation and ignition.—5. *Silica:* From crude potash, when that substance is used for the precipitation, or from the crucible. Left behind on dissolving the oxide in hydrochloric acid.—

6. *Sesquioxide of Manganese:* Partly left behind when the zinc-oxide is dissolved in dilute nitric acid. Produces a green colour when ignited with carbonate of soda and nitre.—7. *Sesquioxide of Iron:* The solution in hydrochloric acid gives a red colour with sulphocyanide of potassium, and exhibits the other reactions of ferric salts.—8. *Oxide of Lead:* Boiling carbonate of soda extracts this oxide almost completely; the filtrate blackens on the addition of hydrosulphuric acid, and then, on the addition of an acid, gives a precipitate of sulphide of lead. The oxides of copper and cadmium remain undissolved in this process.—The solution of the zinc-oxide in hydrochloric or nitric acid gives a precipitate of lead-sulphate on the addition of a large quantity of sulphuric acid.—9. *Oxides of Cadmium and Copper:* The liquid filtered from the lead-sulphate, or the hydrochloric acid solution of the zinc-oxide freed from lead by boiling with carbonate of soda, gives with hydrosulphuric acid, a yellow or brown precipitate, which must be further examined.—10. *Oxides of Nickel and Cobalt.*—See the methods of Berzelius and Ullgren. (*Jahresb.*, 21, 22, 143 and 145.)

Sublimed and mostly impure zinc-oxide is occasionally obtained, in the form called *Furnace-calamine, Cadmia fornacum, Tatia,* or, when it is whiter, *Pompholyx*, in the preparation of brass and in the smelting of zinkiferous ores in the smelting-furnace, in the shaft of which it collects. A furnace-calamine from an iron-smelting furnace examined by Anthon (*J. pr. Chem.* 9, 4), was found to contain zinc-oxide 74·9, lime 1·7, ferric oxide 13·9, lead- and cadmium-oxide 0·8, silica, with a small portion of cobalt-oxide 2·5, quartz adventitiously mixed 4·3 (loss 1·9).

Properties. Crystalline system, the hexagonal. *Red zinc-ore* occurs in six-sided prisms, of specific gravity 6·2. (Vernon.) In furnace-calamine, Koch found crystals having the forms of *Figs.* 131 (some more obtuse, others more acute), 132, 135, 137, and 138.—At the zinc-smelting works at Filisur in the Grisons, there are found sublimed in the upper parts of the crucibles in which the zinc is melted, amber-coloured, transparent, hard, shining, six-sided prisms (*Figs.* 135 and 138), which have a density of 6·0, yield a white powder becoming yellow when heated, and consist of zinc-oxide with a trace of sulphide. (Vernon, *Phil. Mag. Ann.* 7,401).—In the cracks of the earthen tubes in which zinc is distilled, Laurent and Holms (*Ann. Chim. Phys.* 60, 333) found microscopic six-sided prisms. When 1 part of zinc-oxide is heated to commencing redness with from 4 to 6 parts of potash-hydrate, and the product exhausted with water, dingy yellow needles of zinc-oxide are left behind. (Becquerel, *Ann. Chim. Phys.* 51, 105.)—Specific gravity of zinc-oxide =5·600 (O. Boullay), 5·7344 (Karsten).—¶ According to Brooks (*Pogg.* 74, 439) the specific gravity of pure crystallized zinc-oxide is between 5·61 and 5·65.—Crystalline zinc-oxide, deposited in an earthen retort used for the distillation of zinc, was found by W. and T. Herapath to be aggregated in acuminated masses of small, shining, transparent crystals, which appeared to be right rhombic prisms; their specific gravity was 5·53. When treated with acids, they yielded, without effervescence, from 88·5 to 92 per cent. of zinc-oxide, and an insoluble crystalline residue consisting of ZnO, SnO^2. (*Chem. Soc. Qu. J.*, I. 42.) ¶

The oxide prepared by (1) has the form of white flakes, or, after levigation, that of a white powder The oxide prepared by (2) is a white, loosely-coherent powder, having a slight tinge of lemon-yellow.

Both varieties acquire a lemon-yellow colour when heated, but lose it again on cooling. The change of colour is not accompanied either by absorption or by evolution of oxygen. The yellowish tint which the second variety, whether it has been gently or strongly ignited, exhibits in the cold, is sometimes attributed to the presence of foreign oxides. It is, however, exhibited even by the perfectly pure oxide; and, if the oxide formed by the combustion of zinc be dissolved in acids, precipitated and ignited (Jansen), or dissolved in nitric acid, evaporated and ignited (Schindler), it likewise acquires this yellow tinge; in fact, the oxide prepared by precipitation and ignition, and which is probably less dense than the other variety, appears to possess this colour as an essential character.—The carbonate precipitated from cold solutions, yields on ignition, a lighter oxide than that which is precipitated hot; and this lighter oxide acquires a brighter yellow colour by ignition; if on the contrary, the oxide is denser from the presence of sulphuric acid, chlorine, and soda, it does not exhibit this tinge of yellow when cold. (Wackenroder.)—The oxide (2) loses its yellowish tint by strong ignition on platinum. (Schindler.)—Zinc-oxide emits a strong light in the blowpipe flame. It is volatile at a strong white heat.

				Berzelius.		Gay-Lussac.	Jacquelain.
		Proust.	*earlier.*	*later.*			
Zn	32·2	80·1	80	80·39	80·1	80·38	80·534
O	8·0	19·9	20	19·61	19·9	19·62	19·466
ZnO	40·2	100·0	100	100·00	100·0	100·00	100·000

	Thomson.	Döbereiner.	Clem. & Désormes.
ZnO	80·54	81·64	82·15
O	19·46	18·36	17·85
ZnO	100·00	100·00	100·00

Decompositions. By potassium, at a gentle heat, and without combustion. By charcoal at a strong red heat, yielding zinc vapour and carbonic oxide gas. If the zinc-oxide is in excess, carbonic acid gas is likewise formed. (Gm.) By carbonic oxide gas, with difficulty, yielding zinc and carbonic acid gas. (Dulong, Despretz, *Ann. Chim. Phys.* 43, 222; also *Pogg.* 18, 159; Gm.) By hydrogen gas, with great difficulty, yielding metallic zinc and water. (Despretz, Wackenroder, Gm.) By sulphur, the products being sulphide of zinc and sulphurous acid.

Combinations.—a. With water.—Hydrate of Zinc-oxide, or Zinc-hydrate.—Ignited zinc-oxide immersed in water does not enter into combination with it. (Wackenroder.)—*Preparation.* 1. When zinc in contact with iron is immersed in aqueous ammonia for eight days, and the evolved hydrogen allowed to escape through a gas-delivery tube, there are deposited on the zinc and on the sides of the glass, small, transparent, colourless, rhombic prisms, which have a glassy lustre, are permanent in the air, and leave zinc-oxide when ignited. (Schindler.) Nicklès has likewise found that hydrated zinc-oxide crystallizes in right rhombic prisms. (*N. Ann. Chim. Phys.* 22, 31.)—2. Nitrate of zinc-oxide is precipitated by an insufficient quantity of potash, and the light, flocculent precipitate, washed till the water no longer dissolves out any zinc-salt. (Bonnet.) If an excess of potash is used, the precipitate contains potash. Sulphate and hydrochlorate of zinc-oxide yield an impure hydrate. (Bonnet.)

	Crystallized.		Schindler (1.
ZnO	40·2	81·71	81·62
HO	9·0	18·29	18·38
ZnO, HO	49·2	100·00	100·00

b. With Acids, forming the SALTS OF ZINC-OXIDE or ZINC-SALTS. The affinity of zinc-oxide for acids is considerable. The salts are colourless, unless the acid itself is coloured. They are mostly soluble in water; the solutions redden litmus, and have a disagreeable, rough, and somewhat ferruginous taste. They exert an emetic action. When ignited, they give up all their acid, provided it is volatile; the sulphate, however, gives up its acid with difficulty. They produce a white deposit on charcoal in the inner blowpipe flame; when moistened with nitrate of cobalt and ignited, they yield a green residue.—Free hydrosulphuric acid, added to a solution of zinc-oxide in the weaker acids, such as acetic acid, precipitates the whole of the zinc in the form of white hydrated sulphide; from solutions of zinc-oxide in the stronger acids, such as sulphuric, nitric, and hydrochloric acid, sulphuretted hydrogen precipitates nothing, if the acid is in great excess, and only a portion of the zinc, if the acid is not in excess. Hydrosulphate of ammonia precipitates zinc-salts completely; the precipitated zinc-sulphide is insoluble in hydrosulphate of ammonia, and likewise in caustic ammonia, potash, and soda, and their carbonates, and only slightly soluble in acetic acid. With 1 part of zinc in the form of sulphate dissolved in 10,000 parts of water, hydrosulphate of potash still gives flakes; in 20,000 parts of water, only a faint opalescence. (Lassaigne.)—Caustic alkalis throw down a white gelatinous hydrate of zinc-oxide, soluble in excess of ammonia, potash, and soda. The alkaline solution thus formed gives a white precipitate with hydrosulphuric acid; but the precipitation is not complete till after some time.—Zinc-salts dissolved in water give, with carbonate of ammonia, a white gelatinous precipitate of carbonate of zinc-oxide, soluble in excess of the re-agent; with carbonate of potash or soda, they form a similar precipitate, which, however, is insoluble in excess of the re-agent, but is dissolved on passing chlorine through the liquid. If the zinc-solution is mixed with sal-ammoniac, carbonate of potash or soda gives a precipitate only after long boiling. (H. Rose.) A solution of zinc-vitriol, containing only 1 part of zinc in 10,000 parts of water, still gives slight flakes with carbonate of potash or soda; with 20,000 parts of water, the precipitate appears after some time only. (Lassaigne.) Bicarbonate of potash or soda precipitates zinc-salts with copious evolution of carbonic acid.—Zinc-salts are not precipitated by carbonate of lime (Fuchs, *Schw.* 62, 191); the carbonates of baryta, strontia, lime, and magnesia, do not precipitate them at ordinary temperatures, but completely at a boiling heat. (Demarçay, *Ann. Pharm.* 11, 240.)—Phosphate of soda gives a white precipitate, soluble in ammonia and in potash.—Oxalic acid precipitates zinc-oxide in the form of a white oxalate, and, according to Thomson, the precipitation is complete. If the solution is very dilute, the turbidity does not appear till after some time. (H. Rose.) The precipitate is produced, even when the zinc-salt contains a large excess of acid, provided it be considerably diluted. The precipitated oxalate is soluble in ammonia and in potash.—Zinc-salts give, with ferrocyanide of potassium, a white gelatinous precipitate, and with the ferricyanide, a yellowish red precipitate, both soluble in hydrochloric acid: 1 part of zinc in the form of sulphate, dissolved in 10,000 parts of water, gives a slight turbidity

with ferrocyanide of potassium; in 20,000 parts of water, a very slight turbidity; with the same quantity of salt in 80,000 parts of water, the turbidity does not appear till after 5 or 10 minutes. (Lassaigne.) Tincture of galls precipitates the basic salts of zinc, or those which contain a weak acid, even when the solutions are very dilute. (Schindler.) Zinc-salts are not precipitated by heavy metals, or by sulphite of ammonia.—Those zinc-salts which are insoluble in water, dissolve in hydrochloric acid and in a hot aqueous solution of sal-ammoniac.

c. With alkalis and with certain oxides of the heavy metals.

C. Peroxide of Zinc?

Thénard (*Ann. Chim. Phys.* 9, 55) obtained this compound by treating hydrated zinc-oxide with aqueous peroxide of hydrogen at 0°. It forms a gelatinous mass, which, even at ordinary temperatures, and still more at 100° gives off oxygen gas, and dissolves in acids, forming a salt of zinc-oxide mixed with peroxide of hydrogen. Possibly, a compound of zinc-oxide with peroxide of hydrogen.

Zinc and Hydrogen.

A. *Hydride of Zinc?*—(*Vid.* Ruhland, *Schw.* 15, 418.)

B. *Zincuretted Hydrogen Gas?*—Vauquelin obtained this gas by igniting 4 parts of roasted blende with 1 part of charcoal powder—Colourless, lighter than air, heavier than hydrogen. Has a faint but unpleasant odour. When set on fire by a flaming body, it burns in the air with a bluish and yellowish white flame, forming white clouds of zinc-oxide, and depositing a small quantity of metallic zinc. When mixed with chlorine, it explodes by contact with flame, producing hydrochloric acid and chloride of zinc. Not decomposed by nitric acid or by easily reducible metallic salts. Not absorbed by water. Does not combine with salifiable bases.

Zinc and Carbon.

A. *Carbide of Zinc?*—Nearly all the zinc of commerce contains carbon. —The black powder which is left behind in the distillation of cyanide of zinc, and which, when thrown on red-hot coals, burns and forms oxide of zinc, is regarded by Berzelius as carbide of zinc.

B. Carbonate of Zinc-oxide or Zinc-Carbonate,—*Carbonate of Zinc.**—Ignited zinc-oxide does not absorb carbonic acid from the air (Schindler); but if carbonic acid gas be passed through ignited zinc-oxide

* The longer terms, carbonate of zinc-oxide, nitrate of silver-oxide, &c., are those which accord most strictly with the received nomenclature of the alkaline salts, such as carbonate of soda, nitrate of lime, &c.; the shorter terms, zinc-carbonate, silver-nitrate, &c., are convenient abbreviations of them. The more ordinary terms, carbonate of zinc, nitrate of silver, &c., though not strictly correct in point of form, are nevertheless convenient in the case of metals which, like zinc, lead, and silver, have but one oxide which forms salts. [W.]

diffused through water in such quantity as to form a semifluid mixture, the oxide takes up 4·585 per cent. of carbonic acid and 8·347 water. (Wackenroder.)

a. Octobasic.—Obtained by boiling octobasic sulphate of zinc-oxide with aqueous carbonate of soda. — *b. Quadrobasic.* — By boiling the quadrobasic sulphate with carbonate of soda. (Schindler.)

a.			Schindler.
$8ZnO$	88·94		88·92
CO^2	6·08		6·11
$2HO$	4·98		4·97
$8ZnO, CO^2 + 2Aq.$	100·00		100·00

b.				Schindler.
$4ZnO$	160·8	80·08		80·00
CO^2	22·0	10·96		11·01
$2HO$	18·0	8·96		8·99
$4ZnO, CO^2 + 2Aq.$	200·8	100·00		100·00

c. With 2 At. acid to 5 At. base.—This is probably the composition of *Zinc-bloom.*—1. Produced when zinc covered with water is exposed to the air. (Bonsdorff.)—2. When a zinc-salt is precipitated by monocarbonate of ammonia, potash or soda. In this reaction, carbonic acid is set free; and if the solutions are cold, a quantity of zinc-oxide is dissolved by it in the form of acid carbonate, greater in proportion to the quantity of water present; on boiling, however, the carbonic acid is evolved. It is difficult to obtain the precipitate quite free from alkali and from the acid of the zinc-salt used —*a.* A boiling solution of zinc-sulphate is added to boiling carbonate of soda (or potash), which may be in excess; violent effervescence ensues, and a very soft, loose powder is formed, which resembles *magnesia alba* when dry, and is free from alkaline carbonate, if the boiling be continued for some time after mixture. (Schindler.)—*b.* The solution of 1 At. zinc-sulphate and 1 At. carbonate of soda (or potash) are mixed cold; in this case, the translucent jelly which separates at first is soon transformed, with evolution of carbonic acid, into an opaque powder. If the carbonate of soda is in excess, a portion of it is taken up by the precipitate and cannot be removed by subsequent boiling; the jelly is then stiffer, but does not become pulverulent even after standing for weeks; when washed and dried, it forms a coherent mass which adheres tenaciously to the tongue. (Schindler.)—*c.* The solution of zinc-sulphate is mixed with sal-ammoniac, and carbonate of soda added, in the cold, till a glass rod moistened with hydrochloric acid, gives white fumes when held over the liquid. The precipitate, after being washed and dried at 100° in vacuo, is free from soda and sulphuric acid. (Berzelius, *Jahresb.* 15, 130.) *d.* Solution of zinc-sulphate is precipitated in the cold with a precisely equivalent quantity of carbonate of ammonia. The precipitate, which is crystalline at first, becomes very light after drying. (Wackenroder.)—Solution of zinc-nitrate is precipitated cold by an exactly equivalent quantity of carbonate of soda. (Wackenroder.)—The precipitate obtained by decomposing zinc-salts with alkaline carbonates at ordinary temperatures, is, when recently precipitated, much lighter than that obtained from hot solutions. The former contains originally dicarbonate of zinc-oxide together with a large quantity of water, but loses so much water and carbonic acid in drying, that it becomes identical in composition with the salt precipitated from hot solutions. (Wackenroder.)

White, loosely-coherent powder, resembling *magnesia alba*. Dissolves in 2000—3000 parts of water (in 44642 pts. *Fresenius*), but separates from the solution when heated, and does not re-dissolve on cooling. (Schindler.) According to Wöhler (*Pogg.* 28, 616), this salt is deposited in small shining crystals when an aqueous solution of the compound of zinc-oxide and potash is exposed to the air.—Dissolves readily in a cold aqueous solution of hydrochlorate or nitrate of ammonia (Brett, Wittstein), and disengages ammonia when heated therewith. (L. Thompson.)

			Bonsdorff. (1.)	Schindler. (2, *a*.)	Wackenroder. (2, *a*.)	Schindler. (2, *b*.)	Wackenroder. (2, *b*.)
5ZnO	201	73·90	71·25	73·5	72·68	72·22	72·87
$2CO^2$	44	16·17	14·19	14·6	12·74	15·30	12·70
3HO	27	9·93	14·56	11·9	14·02	12·48	13·93
NaO					0·28		
SO^3					0·28		0·50
	272	100·00	100·00	100·0	100·00	100·00	100·00

	Berzelius. (2, *c*.)	Wackenroder. (2, *d*.)	Wackenroder. (2, *e*.)	Smithson. *Zinc-bloom*.
ZnO	73·35	73·23	73·34	71·4
CO^2	15·94	12·80	12·70	13·5
HO	10·71	13·79	13·96	15·1
NaO			trace	
SO^3		0·18		
	100·00	100·00	100·00	100·0

Berzelius and Wackenroder examined the salt dried at 100°; with respect to the other analyses no such particulars are stated. According to Berzelius, the salt is composed of $5ZnO, 2CO^2 + 3\ Aq. = 2(ZnO, CO^2) + 3(ZnO, HO)$. Schindler prefers the formula: $8ZnO, 3CO^2 + 6\ Aq.$ and Wackenroder gives the preference to $12ZnO, 4CO^2 + 9\ Aq.$ The analyses of Smithson and Bonsdorff give nearly: $3ZnO, CO^2 + 3\ Aq.$—¶ Lefort (*J. Pharm.* 3rd series, 11, 329) gives for the salt obtained by precipitating a zinc-salt with carbonate of soda or potash at a boiling heat, the formula: $8ZnO, 3CO^2 + 6HO$. ¶

d. Bibasic.—Dicarbonate.—Formed by precipitating a solution of zinc-sulphate at ordinary temperatures with sesquicarbonate of soda, washing the precipitate thoroughly, and drying it in the air.—Soft, white powder. (Boussingault, *Ann. Chim. Phys.* 29, 284.) By precipitating from hot solutions, the salt *c* is obtained. (Schindler.)

			Boussingault.
4ZnO	160·8	69·37	70
$2CO^2$	44·0	18·98	19
3HO	27·0	11·65	11
$2(2ZnO, CO^2) + 3Aq$	231·8	100·00	100

			Schindler.
2ZnO	80·4	66·78	67·43
CO^2	22·0	18·27	18·00
2HO	18·0	14·95	14·57
$2ZnO, CO^2 + 2Aq$	120·4	100·00	100·00

e. Monocarbonate.—Found in nature as *Zinc-spar* and *Calamine*. Crystalline system the rhombohedral: *Fig.* 141, 143, 145, and other forms; $r^3 : r^3 = 107° 40'$; $r^1 : r$ *behind* $= 72° 20'$. (Wollaston.) Cleavage

parallel to *r*. Specific gravity, 4·3765 (Karsten), 7·442 (Mohs). Hardness equal to that of apatite. White, transparent. Not fusible before the blowpipe. Turns green when ignited with nitrate of cobalt. Dissolves in acids with effervescence; soluble in caustic potash. According to Schindler, this salt may be obtained artificially, containing, however, a small quantity of water (probably from admixture of salt *d*): 1. By precipitating in the cold a solution of 1 At. zinc-sulphate in ten times its weight of water with a solution of 1 At. bicarbonate of potash or soda. The loose, non-gelatinous precipitate is, after drying, soft, white, and much heavier than the salt *c*. (Berzelius obtained by this process the salt *c*, containing 73 per cent. of zinc-oxide; Lefort obtained by the same process, a salt containing: $3ZnO,CO^2+6HO$),—2. The aqueous solution of the acid salt *f*, when left to evaporate spontaneously, deposits the monocarbonate in the form of a granular powder. (Schindler.)

				Smithson.		Schindler.	
				Somersetshire.	Derbyshire.	(1.)	(2.)
ZnO	40·2	64·63		64·8	65·2	63·05	63·0
CO^2	22·0	35·37		35·2	34·8	33·53	34·9
HO						3·42	2·1
ZnO,CO^2	62·2	100·00		100·0	100·0	100·00	100·0

¶ *Manganiferous Zinc-spar.* The following varieties of zinc-spar from Aachen containing manganese, have been analyzed by Monheim. (*L. & K. Jahresb.* 1848, 1225.) *a*, light-green, rhombohedrous: sp. gr. = 4·03; *b*, dark green: sp. gr. = 3·98, both from Herrenberg; *c*, yellowish white from Altenberg: sp. gr. 4·20.

	a.	*b.*	*c.*
ZnO,CO^2	85·78	74·42	84·92
MnO,CO^2	7·62	14·98	6·80
FeO,CO^2	2·24	3·20	1·58
MgO,CO^2	4·44	3·88	2·84
CaO,CO^2	0·98	1·68	1·58
SiO^2	0·09	0·20	
HO	trace	0·56	1·85
Calamine			
	101·15	98·92	99·57

Ferruginous Zinc-spar; Kapnite? Monheim has likewise analyzed several specimens of the ferruginous zinc-spar from Altenberg described by Breithaupt as a new mineral species under the name of Kapnite. The proportion of iron in these specimens being very variable, Monheim does not regard the mineral as a distinct species, but proposes for the light-green varieties, rich in zinc, the name of *Ferruginous Zinc-spar*, and for the dark-green varieties and those which turn brown by oxidation of the iron, the term *Zinc-ironspar:* (*a*) sp. gr. = 4·09; (*b*) sp. gr. = 4·15; (*c*) sp. gr. = 4·00; (*d*) sp. gr. = 4·04· (*e*) sp. gr. = 4·00; (*f*) sp. gr. not determined.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*
ZnO,CO^2	71·08	60·35	58·52	55·89	40·43	28·00
FeO,CO^2	23·98	32·21	35·41	36·46	53·24	67·00
MnO,CO^2	2·58	4·02	3·24	3·47	2·18	
CaO,CO^2	2·54	1·90	3·67	2·27	5·09	5·00
MgO,CO^2		0·14				
Calamine		2·49	0·48	0·41		
	100·18	101·11	101·32	98·50	100·94	100·00

¶.

f. Acid-salt. Metallic zinc, the hydrated oxide, and the carbonates *a . . . e* are easily soluble in excess of aqueous carbonic acid. (*Comp.* Jahn, *Ann. Pharm.* 28, 119.)

Zinc and Boron.

Borate of Zinc-oxide.—Precipitated on mixing an aqueous solution of zinc-sulphate with borax. White powder, insoluble in water, but soluble in aqueous boracic acid. Turns yellow in the fire, and is converted into a solid, compact, opaque slag. (Wenzel; *comp.* Tannermann, *Kastn. Arch.* 20, 14.)

Zinc and Phosphorus.

A. Phosphide of Zinc.—*a.* When pieces of phosphorus are thrown upon melted zinc, a lead-grey mass is obtained, having the metallic lustre, somewhat ductile, smelling like phosphorus when hammered, and burning like zinc when heated. (Pelletier; *comp.* Landgrebe, *Schw.* 53, 460).—*b.* The silver-white substance with conchoidal fracture which sublimes on igniting 6 parts of zinc with 6 phosphorus and 1 charcoal, or 2 zinc with 1 phosphorus in a glass retort, appears to be richer in phosphorus than the last.—*c.* When phosphuretted hydrogen gas is passed over gently heated chloride of zinc—whereupon hydrochloric acid gas is slowly evolved—and the mass afterwards digested in water, phosphide of zinc remains in blackish particles, which exhibit the metallic lustre, emit a phosphorus flame when heated on charcoal before the blowpipe, and are perfectly insoluble in hydrochloric acid. (H. Rose, *Pogg.* 24, 235.)

B. Hypophosphite of Zinc-oxide.—The solution of zinc in heated aqueous hypophosphorous acid, yields by evaporation in vacuo, indistinct crystals, which, when heated to redness in a retort, swell up strongly, give off non-spontaneously inflammable phosphuretted hydrogen, and leave a residue soluble in hydrochloric acid. (H. Rose, *Pogg.* 11, 92.)

C. Phosphite of Zinc-oxide.—Perchloride of phosphorus dissolved in water and neutralized by ammonia, precipitates a small quantity of this salt from a solution of zinc-sulphate, the rest remaining in solution, and separating when the liquid is boiled. The salt, when heated, swells up strongly, and gives off hydrogen gas, mixed, especially towards the end of the reaction, with phosphuretted hydrogen. 100 parts of the salt dried in vacuo leave, on ignition, 79·43 parts of residue containing 53·38 per cent. of zinc-oxide, and 46·62 phosphoric acid. 100 parts of the dried salt oxidated by nitric acid and ignited, yield 81·4 parts of diphosphate of zinc-oxide. The salt dissolves with difficulty in water. (H. Rose, *Pogg.* 9, 29.)

					H. Rose.
$2ZnO$	80·4	....	42·36	....	43·14
PO^3	55·4	....	29·19	....	29·69
$6HO$	54·0	....	28·45	....	27·17
$2ZnO,PO^3+6Aq.$	189·8	....	100·00	....	100·00

D. Ordinary Phosphate of Zinc-oxide or Zinc-phosphate.—*a. Triphosphate.*—Precipitated on mixing a solution of a zinc-salt with

diphosphate of ammonia, potash, or soda, the supernatant liquid becoming acid. (Mitscherlich.) When dilute solutions of sulphate of zinc-oxide and diphosphate of soda are mixed in the cold, a translucent jelly is at first produced; this, however, soon becomes opaque and aggregates into a fine white crystalline powder. If the solutions are mixed boiling hot, no jelly is produced, but the pulverulent precipitate is formed at once and has the same composition. (Schindler.) The same compound is doubtless formed on digesting carbonate of zinc-oxide with aqueous phosphoric acid not in excess. White, crystalline, tasteless powder. Fuses easily, forming a transparent and colourless glass. Insoluble in water; soluble in acids; likewise in ammonia and in carbonate, sulphate, hydrochlorate, and nitrate of ammonia—in the last three, however, with slight turbidity.

	Anhydrous.				*Hydrated.*			Schindler.
3ZnO	120·6	....	62·81	3ZnO	120·6	....	57·43	.... 57·46
cPO^5	71·4	....	37·19	cPO^5	71·4	....	34·00	.... 33·86
				2HO	18·0	....	8·57	.... 8·82
$3ZnO,cPO^5$	192·0	....	100·00	+2Aq.	210·0	....	100·00	.... 100·14

b. Diphosphate. On mixing a solution of 3 parts of zinc-sulphate in 32 parts of hot water, with a solution of 4 parts of crystallized diphosphate of soda in 32 parts of hot water, this salt is deposited in shining laminæ. (Graham.) In this case, the zinc-sulphate is in excess; in the preparation of salt *a*, it appears to be necessary that the phosphate of soda be in excess. The crystals do not lose water at 100°; but at a temperature below the melting-point of tin, they give off 2 At. water, retaining their lustre; at a red heat they fuse and give off 3 At. water. (Graham, *Ann. Pharm.* 29, 28.)

	Dried.				*Crystallized.*		
2ZnO	80·4	....	50·0	2ZnO	80·4	....	44·97
cPO^5	71·4	....	44·4	cPO^5	71·4	....	39·93
HO	9·0	....	5·6	3HO	27·0	....	15·10
$2ZnO,HO,cPO^5$	160·8	....	100·0	+2Aq.	178·8	....	100·00

c. Acid Phosphate. By dissolving zinc, or the carbonate or phosphate of zinc-oxide in excess of acid and evaporating. Gummy mass which fuses in the fire to a transparent glass. When a small quantity of alkali is added to its aqueous solution, the salt *a* is deposited. (Wenzel.)

E. Pyrophosphate of Zinc-oxide.—By precipitating a zinc-salt with pyrophosphate of soda. The precipitate is decomposed by boiling with ordinary phosphate of soda, yielding ordinary phosphate of zinc-oxide and pyrophosphate of soda. (Stromeyer, *Schw.* 58, 129.) ¶ The salt precipitated as above forms a white bulky mass, which in drying shrinks up like hydrate of alumina. If it be suspended in water, and sulphurous acid gas passed through the liquid, the whole dissolves, and the solution, when boiled, yields the salt in the form of a heavy, white, beautifully crystalline powder consisting of $2(2ZnO,bPO^5)+3Aq$. Both the amorphous and the crystalline salt dissolve in acids and in caustic potash; ammonia likewise dissolves the salt, and alcohol added to the solution throws down a syrupy mass. (Schwarzenberg, *Ann. Pharm.* 65, 151.) ¶

Metaphosphate of Zinc-oxide.—Formed by burning hyposulphophosphate of zinc. Transparent glass, soluble in water. (Berzelius.)

Zinc and Sulphur.

A. Sulphide of Zinc, or Zinc-sulphide.—Found in nature as *Blende*, frequently containing sulphide of iron and sulphide of cadmium. Nöggerath and Bischof (*Schw.* 65, 245) found in an old mine a quantity of zinc-sulphide mixed with washings of the ore, forming a deposit some inches in thickness on the wood-work; it had probably been formed by the reducing action of the wood upon sulphate of zinc-oxide. *Formation.* 1. When sulphur vapour is passed over red-hot zinc, a small quantity of white sulphide is produced. (J. Davy.) When zinc-filings are heated with sulphur, the sulphur volatilizes before combination takes place. The sulphide of zinc, which has a very high melting point, envelops the zinc in the form of a solid crust; hence the imperfect combination. 2. When zinc is heated with cinnabar (the heat must be very strong towards the end of the process) decomposition takes place, with explosion, the sulphur combining with the zinc and the mercury volatilizing. Zinc-filings mixed with pentasulphide of potassium withdraw the sulphur from that compound, and with explosive combustion if heat be applied. (Berzelius.)—3. According to Dehne, oxide of zinc, heated with sulphur, yields a sulphide of zinc which might easily be mistaken for blende. (Despretz, *Ann. Chim. Phys.* 33, 168.)—4. By heating anhydrous sulphate of zinc-oxide with sulphur. (Vauquelin.) The mixture is heated in an earthen retort, first to dull redness, then more strongly; the sulphide of zinc produced is mixed with more or less undecomposed sulphate, which may be extracted by water, or completely converted into sulphide by again igniting the mixture with sulphur. (Gay-Lussac.)—5. Anhydrous sulphate of zinc-oxide is ignited with charcoal or in a charcoal crucible; if, however, a very strong white heat be applied, very little remains in the crucible. (Berthier.) When 100 parts of the dry salt are ignited in a charcoal crucible with 15 parts of charcoal, part of the sulphuric acid escapes in the form of sulphurous acid before the charcoal begins to act strongly, and consequently there is formed a mixture of sulphide and oxide of zinc, the latter of which may be extracted by dilute hydrochloric acid. If a strong white heat be applied, the residue amounts to only 15 per cent. (Berthier, *Ann. Chim. Phys.* 33, 168.) The more quickly the heat is raised to whiteness, the smaller is the quantity of oxide mixed with the sulphide. (Gay-Lussac.)—6. The precipitate formed by hydrosulphuric acid in a solution of a zinc-salt is ignited in a stream of hydrosulphuric acid gas. (Berzelius.)

The native sulphide belongs to the regular system: *Fig.* 2, 3, 4, 6, 8, 13, 14, and other forms. Cleavage easy parallel to *d*. Harder than calcspar. Sp. gr. 3·9—4·07. Transparent, pale yellow. The presence of other metallic sulphides gives it a red, brown, black, or green colour. The artificial sulphide is a white or yellowish, loosely-coherent mass. Sp. gr. 3·9235. (Karsten.) When prepared by (5) it is pulverulent and as white as the oxide. (Berthier.) Fuses only at very high temperatures: not volatile at a white heat.

			Arfvedson.	Thomson.	Proust.
Zn	32·2	66·8	66·34	67·19	85
S	16·0	33·2	33·66	32·81	15
ZnS	48·2	100·0	100·00	100·00	100

When mixed with charcoal and raised to an intense white heat, it volatilizes, doubtless in the form of sulphide of carbon and metallic zinc. (Berthier.) When heated in the air, it oxidates but slowly, evolving sulphurous acid and forming oxide and sulphate. Completely oxidized by fusion with nitre. Decomposed for the most part by evaporation with oil of vitriol. Dissolves in nitric acid, with evolution of nitrous gas and separation of sulphur, and in hot strong hydrochloric acid, with evolution of sulphuretted hydrogen. Decomposes vapour of water slowly at a red heat, more abundantly at a white heat, oxide of zinc being formed and sublimed. (Regnault, *Ann. Chim. Phys.* 62, 380.) When it is heated to redness with carbonate of soda, in equal numbers of atoms, the mass fuses and boils, and yields a yellowish white mixture of sulphide of sodium, oxide of zinc, and undecomposed sulphide of zinc. (Berthier, *Ann. Chim. Phys.* 33, 167.) [For its decomposition with oxide of lead, see *Oxide of Lead.*]

Hydrated Sulphide of Zinc, or *Hydrosulphate of Zinc-oxide.*—The white pulverulent precipitate which hydrosulphuric acid and alkaline hydrosulphates produce with zinc-salts. On passing hydrosulphuric gas very slowly through a solution of zinc-sulphate from which part of the zinc has been already precipitated by that gas, the sulphide is obtained, partly in the form of a dense mass, partly in rhombic laminæ attached thereto; these crystals are yellowish, not hard, and easily cloven. (Schindler.) When hydrochlorate of zinc-oxide mixed with excess of acid is precipitated by sulphuretted hydrogen, the precipitate contains sulphide of zinc in combination with chloride. (Reinsch, *Repert.* 56, 190.) —The white compound is converted by ignition into the yellowish anhydrous sulphide. The sulphide thus formed is mixed, however, with a small portion of oxide, inasmuch as hydrosulphuric acid gas is evolved during ignition. (Schindler.)—Hydrated zinc-sulphide dissolves more readily in nitric or hydrochloric acid than the anhydrous sulphide; dissolving, in fact, without the application of heat: it is also slightly soluble in a large excess of acetic acid. (Wackenroder, *N. Br. Arch.* 16, 133.) While yet moist, it likewise dissolves in aqueous sulphurous acid. (Berthier.)

				Schindler.	Geiger & Reimann.
Zn	32·2	56·30		57·0	59·8
S	16.0	27·97		27·9	29·5
HO	9·0	15·73		15·1	10·7
ZnS, HO	57·2	100·00		100·0	100·0

The compound examined by Schindler was dried at 37·5°; that examined by Geiger & Reimann (*Mag. Pharm.* 18, 25), at 100°. According to Schindler, it loses half its water at 100°, but recovers it on exposure to the air.

B. Oxy-sulphide of Zinc.—When hydrogen gas is passed over 100 parts of anhydrous sulphate of zinc-oxide ignited in a glass tube, the salt is quickly reduced, with formation of sulphurous acid and water; shortly before the end of the reduction, the mass exhibits a swelling movement and a glimmering light, and a small quantity of metallic zinc sublimes. The residue consists of 56 or 58 parts of a straw-yellow powder, containing rather more than 1 At. sulphide of zinc to 1 At. oxide. This compound, when ignited in a stream of sulphuretted hydrogen, is converted into zinc-sulphide and water; hydrochloric acid dissolves it, with evolution of sulphuretted hydrogen. (Arfvedson, *Pogg.* 1, 59.)

Under this head may likewise be included the following compounds, which however contain a larger quantity of sulphide: *a. Volzite.* Warty masses formed of concentric shells; of specific gravity 3·66; pale rose-red or yellowish; slightly translucent. Contains: zinc-sulphide 82·82,—zinc-oxide 15·34,—ferric-oxide 1·84. (Fournet, *Pogg.* 31, 62.)—*b. Furnace-calamine from a Freiberg furnace.* Hollow six-sided prisms or laminar masses; yellow, or, if they contain sulphide of iron or other metallic sulphides, brown and black. Contains 4 At. sulphide of zinc to 1 At. oxide. Gives up the latter to boiling acetic acid. (Karsten, *Schw.* 57, 186.)

C. Hyposulphite of Zinc-oxide.—Formed by digesting aqueous sulphite of zinc-oxide with sulphur in close vessels.—2. By precipitating hyposulphite of baryta with sulphate of zinc-oxide, and filtering. (Rammelsberg.)—3. By passing sulphurous acid gas through water in which freshly precipitated hydrate of zinc-sulphide is diffused: solution takes place with difficulty and is attended with deposition of sulphur. (Rammelsberg, *Pogg.* 8, 442.)—4. By dissolving zinc in aqueous sulphurous acid. The products are sulphite of zinc-oxide which crystallizes out, and hyposulphite which remains in solution. (Mitscherlich, *Pogg.* 8, 442.)

$$2Zn + 3SO^2 = ZnO,SO^2 + ZnO,S^2O^2.$$

If the sulphurous acid becomes very hot by acting on the zinc, sulphuretted hydrogen is evolved, and a portion of the zinc is thereby re-precipitated. (Berzelius; *comp.* Koene, *Pogg.* 63, 245.)—The crystals which Fourcroy & Vauquelin (Fourcroy, *Système* 5, 380) obtained by dissolving zinc in sulphurous acid appear to have been sulphite of zinc-oxide with a portion of hyposulphite adhering to it in the mother-liquid. According to Wöhler (*Jahresber.* 15, 155), zinc, when digested with a saturated aqueous solution of sulphurous acid, forms sulphide of zinc and sulphate of zinc-oxide.—The salt is so easily decomposible that it cannot be obtained in the solid state. If the colourless and inodorous solution, which is not precipitated by alcohol, be evaporated at ordinary temperatures either in the air or in vacuo, white sulphide of zinc is precipitated at a certain degree of concentration, and trithionate of zinc-oxide remains in solution. (Fordos & Gélis, *Compt. rend.* 16, 1070; also *J. pr. Chem.* 29, 228):

$$2(ZnO,S^2O^2) = ZnS + ZnO,S^3O^5.$$

According to Rammelsberg, sulphur is precipitated under these circumstances, and a solution of zinc-sulphate formed.

D. Tetrathionate of Zinc-oxide.—Soluble. (Fordos & Gélis.)

E. Trithionate of Zinc-oxide.—Remains dissolved when a solution of the hyposulphite is evaporated. Decomposed by the slightest rise of temperature in the liquid; so that when aqueous hyposulphite of zinc-oxide is evaporated to dryness, sulphurous acid is evolved and there remains a mixture of sulphide of zinc, sulphur, and sulphate of zinc-oxide. (Fordos & Gélis.)

F. Sulphite of Zinc-oxide or Zinc-sulphite.—Oxide of zinc dissolves in sulphurous acid with evolution of heat, and yields small crystals having a pungent, styptic taste; they are slightly soluble in water, but not in alcohol. (Fourcray & Vauquelin.) The solution when

evaporated yields pearly scales. (A. Vogel, *J. pr. Chem.* 29, 280.) When boiled it deposits a basic salt, the solubility of which diminishes as the boiling is continued. (Berthier, *N. Ann. Chim. Phys.* 7, 82.) The crystals consist of ZnO,SO^2+2Aq. (Fordos & Gélis.) According to Böttinger (*Ann. Pharm.* 51, 405), ignited zinc-oxide dissolves with difficulty in sulphurous acid, and the oxide is deposited on boiling.

G. Hyposulphate of Zinc-oxide.—Formed by precipitating hyposulphate of baryta with an equivalent quantity of zinc-sulphate, then filtering and evaporating. Indistinct crystals, having a very rough taste, permanent in the air, leaving 48·42 per cent. of zinc-sulphate when ignited, very easily soluble in water, and converted into sulphate when the solution is boiled.

	Crystallized.				Heeren.
ZnO	40·2	....	24·19	.....	24·25
S^2O^5	72·0	....	43·32	.....	43·51
6HO	54·0	....	32·49	.....	32·24
ZnO,S^2O^5+6Aq	166·2	....	100·00	.....	100·00

II. Sulphate of Zinc-oxide or Zinc-sulphate.—*Sulphate of Zinc.* *a. Octobasic.*—Precipitated on adding water to a concentrated solution of the bibasic sulphate. Very light precipitate, loosely coherent after drying. When dry, it does not absorb carbonic acid. When kept for a long time under a solution of monosulphate of zinc-oxide, it is converted into the quadrobasic salt. Resolved by gentle ignition into a mixture of zinc-oxide and monosulphate of zinc-oxide, which may be extracted by water. Not soluble in water. (Schindler, *Mag. Pharm.* 31, 181.)

					Schindler.
8ZnO	321·6	....	84·72	....	84·8
SO^3	40·0	....	10·54	....	10·6
2HO	18·0	....	4·74	....	4·6
$8ZnO,SO^3+2Aq.$	379·6	....	100·00	....	100·0

b. Sexbasic.—When NH^3+ZnO,SO^3 is treated with water, this salt is left undissolved in the form of a white powder, which, when heated, gives off 24·12 per cent. of water and afterwards absorbs 8·4 per cent. from the air. (Kane, *Ann. Chim. Phys.* 72, 310.)

	Anhydrous.				*Hydrated.*				Kane.
6ZnO	241·2	....	85·77	6ZnO	241·2	....	64·98	....	64·22
SO^3	40·0	....	14·23	SO^3	40·0	....	10·78	....	10·96
				10HO	90·0	....	24·24	....	24·82
$6ZnO,SO^3$	281·2	....	100·00	+10Aq	371·2	....	100·00	....	100·00

c. Quadrobasic.—1. Formed by heating zinc-vitriol till it is partially decomposed, and boiling the residue with water.—2. By boiling the aqueous solution of zinc-vitriol with metallic zinc or zinc-oxide.—3. By precipitating zinc-vitriol with an insufficient quantity of potash, washing the loosely-coherent precipitate, and dissolving it in boiling water. In all three cases, the solution must be filtered hot, and then the salt will separate as it cools. (A. Vogel.) The second method is the surest; in applying the third method, only a small quantity of potash must be used; a larger quantity throws down a more basic salt. (Kühn, *Schw.* 60, 337.) This salt likewise crystallizes out, when a solution of zinc-vitriol is

placed for some time in contact with metallic zinc, or when a solution of the bibasic sulphate is left to evaporate slowly in a glass with a narrow mouth. (Schindler.) White, shining, opaque scales (A. Vogel); long, soft, flexible, transparent, four-sided needles, bevelled at the extremities like those of zinc-vitriol. (Schindler.) When slowly dried it presents the appearance of a soft powder, greasy to the touch,—but when quickly dried in considerable quantities, it forms a somewhat tenacious, unctuous mass, having a dull and somewhat conchoïdal fracture. (Kühn.) Crystals of this salt which have been dried in the air give up 24·7 per cent. (8 atoms) of water between 100° and 125°, without melting or falling to pieces, while 2 atoms remain. At a low red heat, the salt is resolved into oxide of zinc and the monosulphate, the latter of which may be dissolved out by water. (Schindler.) Scarcely soluble in water either cold or hot, but dissolves in a boiling solution of zinc-vitriol. (Kühn.)

	At.		*a.*		At.		*b.*	
ZnO	4	160·8	73·49		4	160·8	67·91	
SO^3	1	40·0	18·29		1	40·0	16·89	
HO	2	18·0	8·22		4	36·0	15·20	
		218·8	100·00			236·8	100·00	

	At.		*c.*		At.		*d.*	
ZnO	4	160·8	58·95		4	160·8	55·29	
SO^3	1	40·0	14·66		1	40·0	13·76	
HO	8	72·0	26·39		10	90·0	30·95	
		272·8	100·00			290·8	100·00	

According to Schindler, *a* is the salt dried above 100°; and *d* is the salt dried at ordinary temperatures; according to Kühn, *b* is the salt dried somewhat above 100°, and *c* is the salt dried at ordinary temperatures; according to Graham (*Ann. Pharm.* 29, 29), the salt has the composition *b*.

d. Bibasic Salt.—Disulphate.—Obtained in solution: 1. By leaving a concentrated solution of zinc-vitriol for a considerable time in contact with metallic zinc or zinc-oxide.—2. By precipitating the oxide from one half of a concentrated solution of zinc-vitriol, and adding the precipitate to the other half. The solution yields small crystals on evaporation; it is decomposed by rapid boiling, by slow evaporation, or by dilution with a large quantity of water, the salt *c* being deposited. It is precipitated by tincture of galls. Zinc-vitriol, when mixed with this salt, loses its tendency to crystallize. (Schindler.)

e. Monosulphate.—Zinc-vitriol, White Vitriol, Gallitzenstein, Vitriolum album s. Zinci.—Zinc dissolves in heated oil of vitriol with evolution of sulphurous acid, and in dilute sulphuric acid, at ordinary temperatures, with evolution of hydrogen. Not only does pure zinc dissolve more slowly than impure zinc, but according to Barrat (*J. Chim. Med.* 17, 655), the state of aggregation has an influence on the rate of solution. Zinc which dissolves with difficulty, ceases altogether to evolve gas if it be granulated by pouring it into water while in the fused state; but if it be then fused again, and cast in plates, it will yield a considerable quantity of gas.—1 part of oil of vitriol diluted with 80 parts of water, dissolves less zinc when 1 part of nitric acid is added to it than it would without that addition (Bigeon); according to Dobereiner (*J. pr. Chem.* 1, 450), the cause of this difference is, that in the latter case, ammonia is formed, and saturates part of the sulphuric acid; hydrogen is, however,

always evolved, but if a large quantity of nitric acid be added, nitric oxide gas is likewise given off. Oxide of zinc combines with oil vitriol, producing great development of heat. (Cadet, *Taschenb.* 1782, 26.)

The salt is prepared on the large scale by roasting ores containing sulphide of zinc, afterwards exhausting them with water, and evaporating the solution to the crystallizing point. By fusion in its own water of crystallization, stirring in wooden troughs with wooden shovels till crystallization takes place, and subsequent pressing in boxes, commercial zinc-vitriol is made to assume the appearance of loaf-sugar. It is contaminated with the substances mentioned on page 6, and may be purified from all of them, excepting sulphate of magnesia, by the methods detailed on pages 6 and 7. The zinc-vitriol of Goslar contains: ZnO, 15·00; MgO, 5·10; MnO, 3·24; FeO, 0·70; SO^3, 29·04; Aq. 47·00 (loss 0·32.) (Wittstein *Report.* 55, 193.) On the small scale, zinc-vitriol is obtained by dissolving zinc in dilute sulphuric acid. [For the purification, *vid.* pp. 6—8.] The crystals, when heated somewhat below redness, yield the anhydrous salt, which is white, friable, of specific gravity 3·40 (Karsten), and has a styptic and slightly acid taste. When ignited alone, it gives off anhydrous sulphuric acid, sulphurous acid, and oxygen gas, and is converted, first into salt *c*, and afterwards at incipient whiteness, into pure zinc-oxide. When heated to low redness with excess of charcoal, it gives off sulphurous acid and carbonic acid gases in the proportion of 2 vol. SO^2 to 1 vol. CO^2, and leaves zinc-oxide mixed with charcoal and traces of metallic zinc and zinc-sulphide, from which, at higher temperatures, zinc is reduced. If, on the contrary, the mixture be quickly heated to whiteness in a porcelain retort, it evolves at first nothing but sulphurous acid gas; but as soon as the heat becomes strong, the gas evolved consists wholly of carbonic oxide, with a small portion of carbonic acid, and the residue consists of sulphide of zinc. (Gay-Lussac, *Ann. Chim. Phys.* 63, 432; also *J. pr. Chem.* 11, 65.) Hydrogen gas converts the salt at a red heat into oxysulphide of zinc. (Arfvedson.) The salt, when mixed with sulphur and heated in an earthen retort, first to low and afterwards to bright redness, gives off a large quantity of sulphurous acid gas, and leaves sulphide of zinc still mixed with a small quantity of sulphate. (Vauquelin, Gay-Lussac.) The salt, when mixed with an aqueous solution of sal-ammoniac, is converted into sulphate of zinc-oxide and ammonia, and hydrochlorate of zinc-oxide; and with solution of nitre, into sulphate of zinc-oxide and potash and nitrate of zinc-oxide. (Karsten.) By aqueous hydrochloric acid it is simply dissolved, not decomposed. (Kane.)

	Anhydrous.			Wenzel.	Smithson-Tennant.	Thomson.
ZnO	40·2	50·12		46·19	50	52·20
SO^3	40·0	49·88		53·81	50	47·77
ZnO,SO^3	80·2	100·00		100·00	100	99·97

Combinations with Water.—The salt dehydrated by ignition and afterwards moistened with water, combines with the water, producing rise of temperature. (Graham.) When exposed to air saturated with aqueous vapour, it takes up in three weeks rather more than 7 atoms of water of crystallization. (Brandes.) If exposed to the air in summer in the state of fine powder, it absorbs 76·9 per cent. (7 At.) of water in the course of ten days, but no more afterwards. (Blücher.)

a. Mono-hydrated.—Remains behind when the hepta-hydrated salt is ' 'ed in the air at 100°, or in vacuo over oil of vitriol at 20°. (Schindler,

Graham.) Likewise separates in crystalline grains during the cooling of a boiling saturated solution of zinc-vitriol in water. Does not part with its one atom of water at 205°, but gives it up when heated to about 238° (Graham); at this temperature, a small quantity of sulphuric acid is likewise volatilized. (Thomson, *Ann. Phil.* 26, 364; Schindler.)

ZnO	40·2	....	45·07
SO^3	40·0	....	44·84
HO	9·0	....	10·09
$ZnO, SO^3 + Aq.$	89·2	....	100·00

β. *Bi-hydrated.*—1. The crystals of the hepta-hydrated salt give up 31·4 per cent. of water at 50°, and crumble to a white powder. (Schindler.) 2. When a solution of zinc-vitriol supersaturated with sulphuric acid is evaporated at a temperature near 100°, a crust of salt forms on its surface, covered with closely-packed, transparent and colourless crystals, which, when immersed in cold water, soon become opaque (Schindler); so likewise, a concentrated solution of zinc-vitriol, mixed at a boiling heat with sulphuric acid, yields a crystalline powder of the same composition (contaminated only with adhering sulphuric acid), and this, when digested with alcohol of specific gravity 0·856, is converted into the penta-hydrated salt. (Kühn.)—3. The powder of the hepta-hydrated salt is converted by boiling with absolute alcohol into a rough sandy substance consisting of the bi-hydrated sulphate. (Kühn.)

					Kühn. (2)		Kühn. (3)
ZnO	40·2	....	40·94	.....	39·11	....	41·29
SO^3	40·0	....	40·73	.....	41·89	....	41·21
2HO	18·0	....	18·33	.....	19·00	....	17·53
$ZnO, SO^3 + 2Aq.$	98·2	....	100·00	.....	100·00	....	100·03

γ. *With 3½ atoms of Water.*—1. When a concentrated aqueous solution of zinc-vitriol containing a small quantity of free acid is left to itself for some time, it deposits, at 0°—besides crystals of the hepta-hydrated salt—the salt γ in opaque rhombohedrons, which are permanent in the air and, when heated, give off their water without fusing. (Anthon, *J. pr. Chem.* 10, 352; *comp.* Kane, *Ann. Chim. Phys.* 72, 367.)

					Anthon.
2ZnO	80·4	....	35·99	....	36·00
$2SO^3$	80·0	....	35·81	....	36·19
7HO	63·0	....	28·20	....	27·81
$(ZnO, SO^3 + 2Aq.) + (ZnO, SO^3 + 5Aq.)$	223·4	....	100·00	....	100·00

δ. *Penta-hydrated.*—1. A solution of zinc-vitriol evaporated between 40° and 50°, becomes covered with a crust consisting of this salt. (Schindler.)—2. The finely pounded hepta-hydrated salt, boiled with alcohol of specific gravity 0·856, yields a uniform pasty mass, which afterwards solidifies into a hard crystalline substance, having a waxy fracture. Entire crystals of zinc-vitriol immersed in cold alcohol, slowly become opaque throughout their whole substance; in boiling alcohol the change takes place immediately. (Kühn.)

					Kühn. (2)		Schindler. (1)
ZnO	40·2	....	32·11	....	32·05	....	64
SO^3	40·0	....	31·95	....	31·03		
5HO	45·0	....	35·94	....	36·92	....	36
$ZnO, SO^3 + 5Aq.$	125·2	....	100·00	....	100·00	....	100

e. Sex-hydrated.—Separates from the aqueous solution at a temperature above 30°, in oblique rhombic prisms. A crystal of the ter-hydrated salt heated above 52° becomes opaque, because it is thereby converted into an aggregate of small crystals of the sex-hydrated salt. (Mitscherlich.) The correction mentioned in III. 238, applies here also.

9. *Hepta-hydrated.*—The ordinary form of zinc-vitriol. Separates from the aqueous solution at temperatures below 30° (86° F). Large, transparent, colourless prisms belonging to the right prismatic system. *Fig.* 73; $u' : u = 91° 7'$; $u' : m = 135° 33'$; $u' : t = 134° 27'$; u' : *the face above* $it = 128° 58'$; $y : m = 120°$; $i : t = 119° 23'$. Cleavage parallel to *t*. (Brooke, *Ann. Phil.* 22, 437.) Sp. gr. 2·036. (Mohs.) The crystals effloresce slightly in the air; at 100°, they give off 37·315 p. c. (6 At.) of water, and afterwards, when heated to low redness, 6·965 p. c. (Kühn.) When boiling water is poured upon them, they decrepitate and become opaque. (Schindler.) 1 part of the crystals dissolves in 0·923 water at 17·5° (63·5° F.), forming a solution of specific gravity 1·4353 (Karsten); hot water dissolves a larger quantity. Hot alcohol, also, even if absolute, dissolves a trace. (Kühn.)

					Mitscherlich.		Thomson.		Kühn.
ZnO	40·2	....	28·07	....	55·24	....	28·95	....	28·02
SO^3	40·0	....	27·93				27·64	....	27·70
7HO	63·0	....	44·00	....	44·76	....	43·41	....	44·28
ZnO, SO^3 + 7Aq.	143·2	....	100·00	....	100·00	....	100·00	....	100·00

f. Bisulphate of Zinc-oxide.—Obtained by accident. Transparent, colourless, oblique rhombic prisms. *Fig.* 81, with *f*-face and some others. $u' : u = 111°$; $i : u'$ or $u = 106°$; $i : f$, *behind* $= 118°$. Fuses when heated, giving off water containing sulphuric acid, and leaves, on ignition, 40 per cent. of monosulphate. Dissolves with difficulty in cold water, easily in warm water. (Von Kobell, *J. pr. Chem.* 28, 492.)

					Kobell.
ZnO	40·2	....	19·98	....	20·00
$2SO^3$	80·0	....	39·76	....	39·66
9HO	81·0	....	40·26	....	40·34
ZnO, $2SO^3$ + 9Aq	201·2	....	100·00	....	100·00

I. Sulphocarbonate of Zinc.—Zinc-salts give with an aqueous solution of sulphocarbonate of calcium, a yellowish-white precipitate, which, on drying, becomes pale reddish-yellow and translucent. (Berzelius.)

K. Sulphide of Phosphorus and Zinc.—Sulphide of zinc, obtained by precipitating a zinc-salt with hydrosulphate of ammonia, and igniting the precipitate in a current of hydrosulphuric acid gas, is placed in the first of two bulbs blown upon a glass tube, then moistened, by means of a pipette, with liquid protosulphide of phosphorus, and very cautiously heated in a current of hydrogen gas, till the excess of sulphide of phosphorus is expelled. If the red mass should turn white from heating too strongly, the whole must be left to cool till the sulphide of phosphorus has again penetrated the mass, and then the heat may be again applied. (*Vid.* II., 215.)—Fine red powder of the colour of minium. Resolved by distillation below a red heat into sulphide of phosphorus which passes over in the form of a pale-yellow liquid, and white zinc-sulphide which

remains behind. Takes fire readily, and when finally heated to redness, leaves ordinary monophosphate of zinc-oxide in a state of fusion. Dissolves in hydrochloric acid with copious evolution of sulphuretted hydrogen, and separation of red pulverulent $\frac{2}{3}$-sulphide of phosphorus. (Berzelius, *Ann. Pharm.* 46, 150.)

					Berzelius.
2ZnS	96·4	....	43·31	....	45
3P	94·2	....	42·32	....	55
2S	32·0	....	14·37		
$2ZnS, P^3S^3$	222·6	....	100·00	....	100

Zinc and Selenium.

A. Selenide of Zinc.—These elements combine but very imperfectly when fused together, the greater part of the selenium volatilizing, and a mere film of sulphur-yellow selenide of zinc being formed on the surface of the metal; but the combination takes places easily and with explosion, when vapour of selenium is passed over zinc at a red heat.—Lemon-yellow, pulverulent.—Cold dilute nitric acid dissolves the zinc, with evolution of nitrous gas; the selenium, which separates in the first instance, is afterwards dissolved, on the application of heat, in the form of selenious acid. (Berzelius.)

Hydrated Selenide of Zinc, or *Hydroseleniate of Zinc-oxide.*—Aqueous hydroseleniate of potash gives with zinc-salts a pale-red precipitate, which, on exposure to the air, assumes a darker red colour from decomposition of the hydroselenic acid; it is insoluble in water. (Berzelius.)

B. Selenite of Zinc-oxide.—*Monoselenite.* White powder, insoluble in water. When heated, it gives off water, and fuses to a yellow transparent liquid, which on cooling forms a white mass, having a crystalline fracture. At a low white heat, it enters into ebullition, and is converted, with sublimation of selenious acid, into an infusible basic salt, no longer decomposible by heat.

					Muspratt.
ZnO	40·2	....	49·12		
SeO^2	56·0	....	35·08		
2HO	18·0	....	15·80	....	16·66
$ZnO, SeO^2 + 2Aq.$	114·2	....	100·00		

b. Biselenite.—By dissolving *a* in selenious acid. Transparent, fissured, gummy mass, easily soluble in water. (Berzelius.)

¶ *c. Quadroselenite.*—When clean zinc-turnings or plates of zinc are immersed in a somewhat concentrated aqueous solution of selenious acid, the metal soon becomes covered with a thin red layer of reduced selenium, and a solution is formed containing quadroselenite of zinc-oxide. This solution, when evaporated to a syrupy consistence in vacuo over oil of vitriol, and then left at rest for about a week, yields the salt in large yellow crystals very much like those of monochromate of potash. Oblique rhombic prisms, having their terminal edges and frequently also the obtuse lateral edges replaced by planes: generally associated in macled crystals.—Permanent in the air, soluble in water. Solution colourless; has a strong sour taste; not decomposed by acids. Becomes turbid when heated, the salt being resolved into selenious acid and neutral zinc-selenite. A

crystal heated to 30° or 40° undergoes the same change, becoming white and opaque; on increasing the heat, the crystal fuses, and is resolved into water which distils over, selenious acid which sublimes, and a neutral or basic salt which remains behind.

					Wöhler.
ZnO	40·2	....	13·97	....	14·86
$4SeO^2$	224·0	....	76 72	....	76·03
3HO	27·0	....	9·31	....	9·10
$ZnO,4SeO^2+3Aq.$	291·2	....	100·00	....	99·99

May be regarded as a double selenite of zinc and water: thus—

$$ZnO,4SeO^2+3HO = ZnO,SeO^2+3HO,SeO^2.$$

(Wöhler, *Ann. Pharm.* 59, 279.) ¶

C. Seleniate of Zinc-Oxide.—ZnO,SeO^3+7Aq. The crystals of this salt, which belong to the square prismatic system, are isomorphous with those of sulphate and seleniate of nickel-oxide. *Fig.* 37; $e:e''=$ 138° 53′; cleavage parallel to the truncation-face *p*. (Mitscherlich, *Pogg.* 12, 144.)

Zinc and Iodine.

A. Iodide of Zinc.—Zinc and iodine combine readily and with slight evolution of heat, producing a colourless, easily fusible substance, which, when heated, sublimes in beautiful four-sided needles. (Gay-Lussac.) From an aqueous solution evaporated by heat, and afterwards cooled, the iodide of zinc separates in octohedrons (Berthemot, *J. Pharm.* 14, 610); and by slow evaporation over oil of vitriol in a receiver containing air, it crystallizes in anhydrous cubo-octohedrons. (Rammelsberg, *Pogg.* 43, 665.) When heated in the air, it gives off iodine vapour, and is converted into oxide of zinc. (Gay-Lussac.) When exposed to the air at ordinary temperatures, it absorbs water and oxygen, and is decomposed. (Buckner, *Report.* 66, 204.) With oil of vitriol it yields sulphurous acid, iodine, and sulphate of zinc-oxide. With the iodides of the alkali-metals, it forms rapidly deliquescent crystals.

					Rammelsberg.
Zn	32·2	....	20·35	....	20·347
I	126·0	....	79·65		
ZnI	158·2	....	100·00		

Aqueous Iodide of Zinc or *Hydriodate of Zinc-Oxide.*—Iodide of zinc deliquesces in the air. The same solution is formed by keeping zinc and iodine immersed in water till the liquid loses its colour.—Colourless, somewhat acid liquid, containing 24 per cent. of zinc-oxide to 76 per cent. of hydriodic acid. (Gay-Lussac.) The highly concentrated solution [overcharged with oxide?] when diluted with water, deposits hydrated zinc-oxide free from iodine. (Rammelsberg.)

B. Oxy-iodide of Zinc.—If the liquid obtained by long digestion of zinc with iodine and water, be filtered hot, it becomes turbid on cooling, and deposits this compound. (W. Müller, *J. pr. Chem.*, 26, 441.)

C. *Aqueous Biniodide of Zinc* or *Hydriodite of Zinc-oxide.*—The aqueous solution of protiodide of zinc dissolves as much iodine as it already contains, and acquires a brown colour. (Baup.)

D. *Iodide of Zinc-oxide?*—Zinc-oxide heated to 200° in contact with iodine, takes up a certain quantity of that substance, but gives it up again on being treated with an acid. (Grouvelle.)

E. Iodate of Zinc-oxide or Zinc-iodate.—Aqueous iodic acid acts upon zinc with effervescence at first, but the effervescence soon ceases in consequence of the formation of a difficultly-soluble salt. (Connell, *N. Edinb. Phil. J.* 11, 72.) Iodic acid and iodate of potash precipitate zinc-sulphate after a while. (Pleischl.)—The salt is prepared by mixing a solution of 1 At. ordinary zinc-sulphate with 1 At. iodate of soda, evaporating to dryness, and extracting the sulphate of soda with water. (Rammelsberg, *Pogg.*, 44, 563.)—Small crystalline grains, or crystalline powder. When heated, it gives off iodine vapour and oxygen gas, and yields a sublimate of somewhat needle-shaped iodide of zinc, leaving a residue of zinc-oxide, mixed with a very small quantity of iodide which may be extracted by water. (Rammelsberg.) Fuses and detonates slightly on red-hot coals. (Berzelius.) Dissolves in 114 parts of water at 15°, and in 76 parts of boiling water. Soluble in nitric acid and in ammonia. (Rammelsberg.)

	Crystallized.				Rammelsberg.
ZnO	40·2	....	17·93	....	91·78
IO^5	166·0	....	74·04		
2HO	18·0	....	8·03	....	8·22
$ZnO,IO^5+2Aq.$	224·2	....	100·00	....	100·00

Zinc and Bromine.

A. Bromide of Zinc.—Zinc and bromine do not combine even when the metal is heated, and the bromine dropped upon it. (Löwig.)—1. The bromide is obtained by passing bromine vapour over red-hot zinc till the metal is converted into a colourless liquid. (Berthemot.)—2. By dissolving zinc in aqueous hydrobromic acid, the solution being attended with evolution of hydrogen. (Balard)—evaporating to dryness—and subliming the residue. (Löwig.)—Sublimes in white needles, which fuse into a light yellow liquid (Löwig); colourless, according to Berthemot. Taste, sweet and styptic. Decomposed by nitric acid. (Berthemot.)

					Berthemot.
Zn	32·2	....	29·11	.....	29·25
Br	78·4	....	70·89	.....	70·75
ZnBr	110·6	....	100·00	.....	100·00

Hydrated Bromide of Zinc or *Hydrobromate of Zinc-oxide.*—Bromide of zinc deliquesces rapidly in the air (Löwig), and becomes strongly heated by contact with water. (Berthemot.) The colourless solution yields small crystals on evaporation. (Löwig.) When evaporated till a film of salt forms on its surface, it solidifies in a mass of indistinct crystals on cooling. (Berthemot.) When evaporated in vacuo, it does not yield crystals, but solidifies to a very deliquescent mass, presenting an appearance of efflorescence on the surface. (Rammelsberg.)—Bromide of zinc

dissolves in ammonia, hydrochloric acid, acetic acid, alcohol, and ether. (Berthemot.)

Bromine-water slowly dissolves a small quantity of zinc-oxide; the solution has no bleaching power, but contains bromide of zinc and bromate of zinc-oxide. (Balard, *J. pr. Chem.*, 4, 177.)

B. Bromate of Zinc-oxide, or Zinc-Bromate.—By dissolving carbonate of zinc-oxide in aqueous bromic acid, and evaporating, octohedrons with cube-faces are obtained, which are permanent in the air. The crystals effloresce in vacuo over oil of vitriol. They fuse at 100°, but do not part with all their water of crystallization till they are heated to 200°, at which temperature, moreover, they are completely resolved into bromine vapour, oxygen gas, and very loosely coherent oxide of zinc. They dissolve in their own weight of cold water. (Rammelsberg, *Pogg.* 52, 90.)

			Rammelsberg.
ZnO	40·2	18·91	16·44
BrO^5	118·4	55·69	58·31
6HO	54·0	25·40	25·25
$ZnO, BrO^5 + 6Aq.$	212·6	100·00	100·00

Zinc and Chlorine.

A. Chloride of Zinc.—*Butter of Zinc, Butyrum Zinci.*—1. Thin laminæ of zinc introduced into chlorine gas at ordinary temperatures burn with a white light and form chloride of zinc. (H. Davy.) Zinc heated nearly to its melting point in a current of dry chlorine gas, absorbs the chlorine, with vivid emission of sparks. (Berzelius.)—2. The chloride is also formed by heating 1 part of zinc filings with 2 parts of corrosive sublimate. (Pott.)—3. By evaporating to dryness an aqueous solution of zinc-chloride prepared as described below, and heating the residue to redness in a glass tube with narrow aperture. (J. Davy, *Schw.* 10, 331.) At the very high temperature required to dehydrate the salt completely, hydrochloric acid is driven off, and a portion of zinc-oxide remains mixed with the chloride. (Mousson, *Ann. Chim. Phys.*, 69, 240.)—4. By evaporating the solution to dryness, and heating the residue in a retort till the chloride of zinc distils over. (Pott, Brandt.)—5. By distilling 1 part of zinc-oxide with 2 parts of sal-ammoniac, the receiver being charged after a while. (Lesage.)—6. By distilling dehydrated zinc-vitriol with its own weight of common salt. (*Crell Chem. J.*, 1, 116.)

Whitish-grey, semi-transparent, soft like wax; fuses, according to H. Davy, somewhat above 100°; according to J. Davy, just below dull redness, and on cooling becomes first viscid, and then solid. Sublimes in white needles at a white heat. Has a burning and nauseating taste even when dilute. (Papenguth.)—When heated in phosphuretted hydrogen gas, it yields hydrochloric acid gas and phosphide of zinc. (H. Rose.)—With cold oil of vitriol, it suddenly gives off all its hydrochloric acid, and leaves sulphate of zinc-oxide. (A. Vogel.) Forms definite compounds with sal-ammoniac and chloride of potassium.

			J. Davy.	Or:			Wenzel.
Zn	32·2	47·63	50	ZnO	40·2	59·47	57·56
Cl	35·4	52·37	50	Cl—O	27·4	40·53	42·44
ZnCl	67·6	100·00	100		67·6	100·00	100·00

Hydrated Chloride of Zinc or *Hydrochlorate of Zinc-oxide.*—Chloride of zinc deliquesces in the air.—Zinc dissolves in aqueous hydrochloric acid, hydrogen gas being evolved and a colourless solution formed. (*Sch.* 9.) A solution of zinc-sulphate may also be precipitated by chloride of calcium, the filtrate concentrated by evaporation, and the remaining liquid separated from the precipitated gypsum. (Papengath, *Schw. Ann.* 2, 143.)—The solution, evaporated to a syrupy consistence, and mixed with a small quantity of strong hydrochloric acid (because it gives off some of its acid during the evaporation) yields small, highly deliquescent octohedrons. (Schindler.)

	Crystallized.				Schindler.
Zn	32·2	....	42·04	....	39·80
Cl	35·4	....	46·21	....	43·81
HO	9·0	....	11·75	....	16·39
ZnCl + Aq	76·6	....	100·00	....	100·00

Protoxide of tin, hydrated oxide of lead, and protoxide of mercury, added to a boiling aqueous solution of hydrochlorate of zinc-oxide, precipitate all the zinc in the form of oxychloride. (Demarçay, *Ann. Phar.* 11, 251.)

B. Oxychloride of Zinc or Basic Hydrochlorate of Zinc-Oxide. —*a.* When aqueous chloride of zinc is evaporated to a syrupy consistence, hydrochloric acid is given off; and the syrup, on subsequent cooling, solidifies in a gelatinous mass, probably from separation of a still more basic salt, which always re-dissolves when heated. Water added to the syrup throws down a white bulky precipitate, and the filtered liquid gives a precipitate with tincture of galls. (Schindler.) A similar solution precipitable by water is obtained by saturating warm concentrated hydrochloric acid with oxide of zinc.

b. ZnCl,3ZnO.—1. Formed by boiling a concentrated solution of chloride of zinc with oxide of zinc, and filtering; the compound is deposited on cooling.—2. By precipitating hydrochlorate of zinc-oxide with an insufficient quantity of ammonia, and digesting the precipitate in the liquid. By (1) fine pearly octohedrons; by (2) soft, white powder. Dissolves sparingly in water, more abundantly in aqueous chloride of zinc, easily in acids and in caustic ammonia or potash. (Schindler, *Mag. Pharm.* 36, 45.)

					Schindler.
ZnCl	67·6	....	32·78	.....	32·5
3ZnO	120·6	....	58·49	.....	58·8
2HO	18·0	....	8·73	.....	8·7
ZnCl,3ZnO + 2Aq.	206·2	....	100·00	.....	100·0

The compound analyzed by Schindler appears to have been dried at 100°; the compound dried at 38° contains 4 At. water. (Kane.)

c. ZnCl,6ZnO.—1. Separates in the decomposition of NH^3,ZnCl or of NH^3,2ZnCl by water. — 2. Precipitated on adding ammonia to the aqueous solution of chloride of zinc, till a portion of the precipitate is re-dissolved.—White, tasteless powder, insoluble in water. Gives off water and chloride of zinc when ignited, and leaves a residue, from which water extracts chloride of zinc, leaving a compound containing a larger proportion of oxide. (Kane, *Ann. Chim. Phys.* 72, 296.)

Dried at 82°.					Kane.
ZnCl	67·6	....	18·63	.....	19·13
6ZnO	241·2	....	66·48	.....	65·85
6HO	54·0	....	14·89	.....	15·02
ZnCl,6ZnO + 6Aq.	362·8	....	100·00	.....	100·00

The compound, when dried at ordinary temperatures, contains 23·5 per cent. (10 At.) of water; when dried at a high temperature, it absorbs from the air 15 per cent. (4 At.) of water, which cannot be driven out at 100°. (Kane.)

d. ZnCl,9ZnO.—1. Precipitated on diluting the syrup *a* with water. —2. By precipitating aqueous zinc-chloride with an insufficient quantity of ammonia and filtering immediately: the compound thus formed contains, however, a small quantity of ammonia. (Schindler.)—3. By adding potash to aqueous zinc-chloride, till the mixture begins to exhibit an alkaline reaction. (Kane.)—Very soft, white powder. Not perfectly freed from chlorine by boiling with carbonate of potash. Converted into the compound *b* by digestion with aqueous zinc-chloride. Insoluble in water, less soluble in ammonia than *b*, but easily soluble in acids. (Schindler.)

					Schindler.
ZnCl	67·6	....	14·81	.....	14·41
9ZnO	381·8	....	79·27	.....	79·88
3HO	27·0	....	5·92	.....	5·71
ZnCl,9ZnO + 3Aq.	456·4	....	100·00	.....	100·00

The salt obtained by (3) contains 5·92 per cent. of chlorine, and 22·68 (14 At.) water; after perfect drying, it absorbs 4 atoms of water from the air.

C. Hypochlorite of Zinc-oxide or Zinc-hypochlorite.—The solution of zinc-oxide in aqueous hypochlorous acid, decomposes spontaneously, if it contains excess of acid, into chlorine gas, chloride of zinc, and chlorate of zinc-oxide; and even when the zinc-oxide is in excess, the solution cannot be evaporated without decomposition. When heated, it gives off hypochlorous acid, probably mixed with a small quantity of free oxygen, and deposits a white, pearly oxychloride, which decomposes spontaneously into chloride of zinc, chlorate of zinc-oxide, oxygen gas, and a small quantity of chlorine gas. (Balard.) Zinc-vitriol mixed with excess of hypochlorite of lime, gives a precipitate consisting of zinc-oxide and sulphate of lime, and a liquid which contains no zinc-oxide, but hypochlorite of lime with excess of acid. (Balard.)—1 At. chlorine in the state of aqueous solution dissolves 1 At. oxide of zinc. The transparent and colourless solution bleaches tincture of indigo strongly, even after a quarter of an hour's boiling. (Grouvelle, *Ann. Chim. Phys.* 17, 37.) The solution is resolved by distillation into hypochlorous acid, which passes over in small quantity, chloride of zinc which remains dissolved, and oxychloride of zinc which separates in the solid state. (Balard.)

D. Chlorate of Zinc oxide or Zinc-chlorate.—1. Formed by dissolving carbonate of zinc-oxide in aqueous chloric acid. Metallic zinc dissolves in the acid without any [or with slight] effervescence, and forms hydrochlorate and chlorate of zinc-oxide.—2. By passing gaseous fluoride of silicium through water in which finely divided carbonate of

zinc-oxide is diffused—boiling the filtered liquid with an equivalent quantity of chlorate of potash—and filtering from the precipitated silico-fluoride of potassium. (O. Henry, *J. Pharm.* 25, 269.)—Chlorate of zinc-oxide crystallizes apparently in octohedrons; tastes very rough.—When thrown on red-hot coals, it is decomposed, with a yellowish light, but without actual detonation. In contact with sulphuric acid it assumes a yellowish colour, and emits an odour of chloric oxide, but does not precipitate a solution of nitrate of silver. Soluble in water and alcohol. (Vauquelin, *Ann. Chim.* 95. 113.)—Contains ZnO,ClO^5+6Aq. (Wächter, *J. pr. Chem.* 30, 321.)

E. Perchlorate of Zinc-oxide or Zinc-perchlorate.—1. By precipitating perchlorate of baryta with zinc-vitriol, and concentrating by evaporation. (Serullus, *Ann. Chim. Phys.* 46, 305.)—2. Obtained like chlorate of zinc-oxide, method 2. The carbonate of zinc precipitated by excess of carbonate of soda from 5 parts of zinc-vitriol, is to be treated, after conversion into silico-fluoride of zinc, with 4 parts of perchlorate of potash. The filtrate, when evaporated to a syrup, and then left in a warm place, deposits crystals. (O. Henry.)—Prisms united in tufts; deliquescent; soluble in alcohol. (Serullas.)

Zinc and Fluorine.

A. Fluoride of Zinc.—Hydrofluate of potash mixed with solution of zinc-vitriol produces a gelatinous precipitate, which by drying is converted into a white tasteless powder. The same compound is obtained by digesting aqueous hydrofluoric acid with excess of zinc. (Gay-Lussac and Thénard.) From its solution in aqueous hydrofluoric acid, this compound separates, on evaporation, in small, white, opaque crystals, having the taste of zinc-salts. It dissolves sparingly in pure water, somewhat more freely in water containing hydrofluoric acid, and likewise in nitric or hydrochloric acid; easily in aqueous ammonia. With the fluorides of the alkali-metals, it forms colourless, sparingly soluble compounds.

Aqueous Hydrofluate of Zinc-fluoride or *Acid Hydrofluate of Zinc-oxide.*—Formed by dissolving fluoride of zinc in aqueous hydrofluoric acid, or by dissolving zinc in excess of aqueous hydrofluoric acid, the reaction being attended with evolution of hydrogen. (Scheele, Gay-Lussac and Thénard.)

B. Fluoboride of Zinc or Hydrofluate of Boracic acid and Zinc-oxide.—ZnF,BF^3.—By dissolving zinc in aqueous hydrofluoboric acid (II, 364) till no more hydrogen is evolved at ordinary temperatures. The solution, when evaporated, leaves a syrup, which solidifies on cooling and deliquesces when exposed to the air.

Zinc and Nitrogen.

A. *Nitride of Zinc?*—A long glass trough contains water and pieces of sal-ammoniac; into one end of this trough there dips a platinum wire connected with the negative pole of a six-pair Grove's battery; into the other, a ball of zinc connected with the positive pole. A spongy, foliated mass, of the colour of graphite, then collects on the negative

wire; this mass grows, and rises to the surface from the buoyancy of the adhering gas-bubbles. When washed with water on the filter, and then dried at a gentle heat, it appears grey, without metallic lustre; has a density of 4·6, and conducts electricity.—5 grains of this substance yield, when ignited, 0·73 cub. in. of a mixture of between 3 and 4 vol. nitrogen gas to 1 vol. hydrogen. The last portions of gas evolved appear to consist chiefly of hydrogen, derived apparently from the decomposition of the adhering water: for moisture is likewise deposited in the tube. The ignited residue exhibits contraction, but without change of colour.—Nitride of zinc dissolves like zinc in aqueous acids, but the hydrogen evolved contains a small quantity of nitrogen. (Grove, *Phil. Mag. J.* 19, 98; also *Pogg.* 54, 101.)

B. NITRATE OF ZINC-OXIDE, or ZINC-NITRATE.—*a. Octobasic.*—Formed by heating the salt *c* till it becomes nearly solid. (Grouvelle, *Ann. Chim. Phys.* 19, 137.) The salt *c*, when heated till part of the acid is driven off, retains its transparency at first. [The mass dissolves partially on cooling, leaving a white residue consisting of a basic salt.] If a larger quantity of acid be driven off, the melted mass appears turbid; and if treated with water after cooling, leaves a yellowish residue, consisting of the salt *a*. (Schindler.)—2. By precipitating the salt *c* with an insufficient quantity of ammonia. (Grouvelle.) The precipitate contains a small quantity of ammonia. (Schindler.)

				Grouvelle (1.)	Schindler (1.)	Grouvelle (2.)
8ZnO	321·6	81·71		81·69	81·70	78·13
NO^5	54·0	13·72		13·75	13·76	13·13
2HO	18·0	4·57		4·56	4·54	8·74
8ZnO, NO^5 + 2Aq.	393·6	100·00		100·00	100·00	100·00

The salt obtained by (2) contains 4 At. water. (Grouvelle.)

b. Quadrobasic. The salt *a* digested with the solution of *c* swells up, turns white, and forms a loose powder when dry. (Schindler.)

			Schindler.
4ZnO	160·8	69·07	68·90
NO^5	54·0	23·19	23·41
2HO	18·0	7·74	7·69
4ZnO, NO^5 + 2Aq	232·8	100·00	100·00

The aqueous solution of *c*, boiled with oxide of zinc, does not take up any of that compound. (Schindler.)

¶ Gerhardt has obtained a basic nitrate of zinc-oxide which crystallizes in prismatic needles, and contains 4ZnO, NO^5 + 3HO. (*J. Pharm.* 3e *ser.* 12, 61.) ¶.

c. Mononitrate. Nitric acid rapidly dissolves zinc, producing great heat, and evolving nitrogen, nitrous oxide, and nitric oxide. (II. 374 and 397.) The salt crystallizes from very concentrated solutions in transparent, colourless, flattened, striated, four-sided prisms, with four-sided summits: it has a styptic taste. Fuses when heated, and at 100° gives off 28 p.c. (3 At.) water; the remaining 3 atoms are not evolved till a temperature is attained at which the nitric acid itself is driven off. (Graham.) The acid is first evolved in its entire state, together with the water; afterwards in the form of hyponitric acid vapour and oxygen

gas. (Schindler.) Detonates with a red flame on glowing coals. Deliquesces in the air; dissolves readily in water and alcohol. Hydrated oxide of lead boiled with the solution precipitates the zinc completely in the form of a basic salt. (Demarçay.)

	Crystallized.			Graham.	Schindler.
ZnO	40·2	27·12		26·94	25·6
NO^5	54·0	36·44			34·5
6HO	54·0	36·44			39·9
$ZnO, NO^5 + 6Aq.$	148·2	100·00			100·0

According to Graham (*Ann. Pharm.* 29, 17) and Millon (*Compt. rend.* 1 4, 905), the crystals contain 6 At. water; Schindler's analysis gives 7 atoms.

C. Zinc-oxide with Ammonia.—1. Hydrated zinc-oxide dissolves easily in aqueous ammonia. The ignited oxide does not dissolve at all in ammonia, according to Firnhaber; according to Schindler, it is but very sparingly soluble, but its solubility is greatly increased by traces of different ammonia and potash salts. The most efficient salts in this respect are the phosphates; then follow the arseniates, hydrochlorates, sulphates, nitrates, acetates, carbonates, tartrates, citrates, and, lastly, the sulphites. Succinic and benzoic acid favour the solution only when the ammonia is very dilute; boracic, hydriodic, chloric, arsenious, oxalic, and gallic acid, when digested with zinc-oxide and ammonia, do not promote the solution of the oxide, but combine with it, together with a small quantity of ammonia. For instance, on adding to ammonia in which zinc-oxide is diffused, a few drops of phosphate of ammonia or potash, the zinc-oxide is immediately dissolved, especially if heat be applied. (Schindler.) Hence may perhaps be explained the fact observed by Firnhaber (*Schw.* 42, 246), *viz.* that zinc-oxide precipitated by ammonia from a solution of the sulphate [the precipitate contains sulphuric acid], dissolves readily in ammonia, even after ignition.—2. Zinc immersed in ammonia and placed in contact with iron dissolves slowly, with evolution of hydrogen, and forms the compound under consideration. (Runge.) By this process, without any admixture of acid, a highly concentrated solution may be obtained; 100 parts of such a solution, which, after the removal of the metallic iron and zinc, had already deposited crystals of hydrated zinc oxide, was found to contain 3·95 parts (1 At) zinc-oxide to 7·68 parts (rather more than 4 At.) ammonia. (Schindler.) The zinc likewise dissolves without the presence of the iron, but more slowly. The solution is colourless; if concentrated, it becomes turbid on dilution with a considerable quantity of water. The solution obtained by (2) may be mixed with 15 times its bulk of water without producing turbidity, but with a larger quantity of water, it gives a coagulated, and with a still larger quantity, a pulverulent precipitate. (Schindler.) The solution (1), when it evaporates in the air, yields needles [probably consisting of carbonate of zinc-oxide and ammonia], and, when evaporated in the sand-bath, leaves an inodorous mass, soluble in water, and evolving ammonia when treated with potash. (Wittstein, *Repert.* 57, 60.) The solution, when evaporated, leaves oxide of zinc containing small quantities of ammonia and carbonic acid. (Bonnet.) Baryta, strontia, and lime-water added to the solution throw down a portion of the zinc-oxide in combination with the earthy alkali. (Berzelius.)

D. Carbonate of Zinc-oxide and Ammonia. — *Zinco-ammonic Carbonate.*—*a.* 1. Zinc-filings and oxide of zinc dissolve readily in aqueous carbonate of ammonia, the former with brisk effervescence, the latter with evolution of heat. The solution yields, on evaporation, white crystals having a silky lustre. The saturated solution is rendered turbid by excess of water, and gives a white precipitate with acids, and a grey precipitate with tincture of galls. (Lassonne, *Crell. Chem. J.* 5, 59; Roloff, *A. Gehl.* 6, 443.) The solution becomes somewhat turbid on dilution with water, in consequence of the precipitation of a compound [probably *b*] richer in oxide. (Bonnet.)—2. When hydrochlorate of zinc-oxide is dropt into excess of ammonia, then carbonate of ammonia added, and the mixture exposed to the air, there are formed, as the ammonia evaporates, needle-shaped crystals united in stellated masses, insoluble in water, and having a strong ammoniacal odour; they turn milk-white in the air, and continue to evolve ammonia till they are converted into the following compound *b*. (Wöhler, *Pogg.* 28, 616.)

b. White powder, which, when heated, evolves a large quantity of water and carbonate of ammonia, and leaves 62·2 per cent of zinc-oxide. (Wöhler.) When zinc-oxide in excess is digested with aqueous carbonate of ammonia, a crystalline powder is obtained. (Bonnet.)

E. *Boride of Nitrogen and Zinc ?*—2 parts of vitrefied boracic acid and 5 parts of cyanide of zinc heated to whiteness for an hour in a closed charcoal crucible yield a white mass. This mass imparts a green colour to the outer blowpipe flame, but without melting; burns with a pale blue light when thrown into fused chlorate of potash; gives off a large quantity of ammonia when heated with hydrate of potash; and is not decomposed by chlorine, even at a red heat. (Balmain, *Phil. Mag. J.* 21, 270.)

F. Ordinary Phosphate of Zinc-oxide and Ammonia.—*Zinco-ammonic Phosphate.*—Formed by adding a solution of ordinary phosphate of ammonia mixed with excess of ammonia to a solution of zinc-vitriol, and digesting till the precipitate has lost its flocculent character and become crystalline, and the excess of ammonia is evaporated—then washing the precipitate, pressing it between folds of bibulous paper, and drying it. Instead of phosphate of ammonia, phosphate of soda mixed with ammonia may be used, but then the washing is difficult. White powder, which, on ignition, yields 79·33 per cent. of zinc-oxide. Insoluble in water, but soluble in acids, ammonia, potash, and soda. (Bette, *Ann. Pharm.* 15, 129.)

	Calculation 1.	
NH^3	17·0	8·68
$2ZnO$	80·4	41·06
cPO^5	71·4	36·47
$3HO$	27·0	13·79
$NH^4O,2ZnO,cPO^5+2Aq.$	195·8	100·00

	Calculation 2.		Bette.
NH^3	17·0	7·20	8·65
$3ZnO$	120·6	51·10	47·55
cPO^5	71·4	30·26	31·78
$3HO$	27·0	11·44	12·02
$NH^4O,3ZnO,cPO^5+3Aq.$	236·0	100·00	100·00

Calculation 1 corresponds to the manganese-salt (IV. 232); calculation 2, which Bette prefers, corresponds to the arseniate (V. 50); neither of them agrees exactly with the analysis.

G. PYROPHOSPHATE OF ZINC-OXIDE AND AMMONIA.—*Zinco-ammonic Pyrophosphate.*—Formed by mixing hydrochlorate of zinc-oxide with a sufficient quantity of sal-ammoniac to prevent precipitation by ammonia, and then adding a mixture of ammonia and pyrophosphate of soda. The precipitate must be washed till the water no longer renders a silver-solution turbid, then pressed between paper, and dried. If the same process be used as for salt F, with the substitution of pyrophosphate of soda for the ordinary phosphate, the resulting precipitate will contain too much zinc-oxide and too little phosphoric acid to exhibit any stoïchiometric relation. The precipitate formed by the first-mentioned process has the appearance of loose flakes. When ignited, it leaves 79·3 per cent. of zinc-phosphate. Contains in 100 parts—ammonia, 5·78; zinc-oxide, 42·43; pyrophosphoric acid, 37·31; water, 14·78,—corresponding to the formula, $2NH^3+6ZnO+3bPO^5+9aq$. (Bette.)

H. METAPHOSPHATE OF ZINC-OXIDE AND AMMONIA.—*Zinco-ammonic Metaphosphate.*—Zinc-vitriol mixed with ammonia is precipitated by a solution of vitrefied metaphosphate of soda, likewise mixed with ammonia. A white precipitate is immediately formed, and subsequently coagulates in a resinous mass. When dry, it forms a white powder. The dry precipitate contains in 100 parts—ammonia 6·50; zinc-oxide 46·45; phosphoric acid 33·68; water 13·37: it is probably a mixture of a double metaphosphate with a double phosphate containing ordinary phosphoric acid. (Bette.)

I. AMMONIO-HYPOSULPHITE OF ZINC-OXIDE.—Aqueous hyposulphite of zinc-oxide supersaturated with ammonia and then mixed with absolute alcohol, deposits this salt in white needles. These crystals, when heated, rapidly evolve a large quantity of ammonia, yield a sublimate of sulphite of ammonia and a very small quantity of sulphate of ammonia, and leave a mixture of sulphide of zinc and sulphate of zinc-oxide. They are decomposed by water, with separation of flocculent zinc-oxide. (Rammelsberg, *Pogg.* 56, 62.)

	Crystallized.			Rammelsberg.
NH^3	17·0	....	16·16	
ZnO	40·2	....	38·21	39·62
S^2O^2	48·0	....	45·63	
NH^3+ZnO,S^2O^2	105·2	....	100·00	

K. AMMONIO-HYPOSULPHATE OF ZINC-OXIDE.—Warm aqueous ammonia saturated with hyposulphate of zinc-oxide, yields small crystals on cooling. These, when heated in a retort, yield free ammonia, a sublimate of sulphite and sulphate of ammonia, and leave a residue consisting of sulphate of zinc-oxide with a small quantity of sulphide of zinc. (Rammelsberg, *Pogg.* 58, 297.)

	Crystallized.			Rammelsberg.
$2NH^3$	34·0	....	23·26	22·53
ZnO	40·2	....	27·50	27·50
S^2O^5	72·0	....	49·24	
$2NH^3+ZnO,S^2O^5$	146·2	....	100·00	

L. QUADROBASIC ZINC-SULPHATE WITH AMMONIA.—The flowers of zinc met with in commerce sometimes consist of this salt. It is precipitated when a boiling solution of zinc-vitriol is supersaturated with

ammonia, and the boiling continued till the liquid no longer smells of ammonia. (Schindler, *Repert.* 31, 20.)

			Schindler.
$2NH^3$	34·0	12·56	12·00
$4ZnO$	160·8	59·38	59·33
SO^3	40·0	14·77	14·66
$4HO$	36·0	13·29	13·33
$2NH^3+4ZnO,SO^3+4Aq$.	270·8	100·00	99·32

The solution of quadrobasic or bibasic zinc-sulphate in ammonia yields small crystals on the addition of alcohol; but on dilution with water, it gives a precipitate in which the quantity of acid and ammonia is less in proportion as the dilution is greater. Aqueous monosulphate of zinc-oxide mixed with a quantity of ammonia just sufficient to re-dissolve the precipitate, is not rendered turbid by small quantities of water; but with larger quantities it forms pulverulent, and with still larger quantities, gelatinous precipitates, containing oxide of zinc, sulphuric acid, and ammonia; when the quantity of water is still further increased, a heavy powder is thrown down consisting of nearly pure hydrated zinc-oxide. A solution of zinc-vitriol supersaturated with ammonia and exposed for some time to the air, deposits quadrobasic sulphate of zinc-oxide, while sulphate of zinc-oxide and ammonia remains in solution. (Schindler, *Mag. Pharm.* 36, 57.)

a is the precipitate formed by mixing zinc-vitriol with an insufficient quantity of ammonia. *b*. With a slight excess of ammonia. (If the addition of ammonia be discontinued as soon as the precipitate ceases to form, the double sulphate of zinc-oxide and ammonia remains in the solution.) *c*. The precipitate obtained by mixing zinc-vitriol with a quantity of ammonia sufficient to re-dissolve the precipitate and then diluting with water. (Bonnet.) [The amount of water is not stated.]

	a.	*b*.	*c*.
NH^3	1·05	4·02	2·42
ZnO	82·27	82·37	81·65
SO^3	16·68	13·61	15·93
	100·00	100·00	100·00

M. Monobasic Zinc-sulphate with Ammonia. — *a*. $5NH^3+2(ZnO, SO^3)$. 100 parts of anhydrous zinc-vitriol rapidly absorb 51·22 parts ($2\frac{1}{2}$ At.) of ammonia, great heat being evolved and the salt swelling up and ultimately crumbling to a white powder. The compound when heated to redness, gives off ammonia with ebullition, yielding a small sublimate of sulphite of ammonia, and a residue which is no longer soluble in water. It dissolves in water with partial separation of zinc-oxide. (H. Rose, *Pogg.* 20, 149.)

b. $2NH^3+ZnO, SO^3$. When ammoniacal gas is passed through a hot saturated solution of zinc-vitriol, till the precipitate is completely re-dissolved, the compound *c* is deposited, on cooling, in flocculent granules. An additional quantity of the salt *c* is obtained by filtering the liquid from the precipitate and either evaporating it to dryness or keeping it warm. If, on the other hand, it be left to evaporate at ordinary temperatures, it yields crystals of *b*. The latter are transparent while moist, but immediately become opaque when dried in the air, passing in fact, without change of form, from $2NH^3+ZnO, SO^3+4Aq$ into $2NH^3+ZnO, SO^3+2Aq$. When kept for awhile at a temperature between 27° and

38°, they give off an additional atom of water and crumble to a white powder, consisting of $2NH^3+ZnO, SO^3+Aq$. The latter, if kept for awhile at 100°, gives off water and ammonia; but to get rid of all the water it is necessary to fuse the salt. If merely heated till it begins to melt, it leaves a gummy mass $= NH^3+ZnO,SO^3+Aq$; after longer fusion there remains NH^3+ZnO,SO^3, constituting 79·13 parts out of 100 parts of the white powder. This compound, when subjected to a continually increasing heat, gives off all its ammonia, and leaves monosulphate of zinc-oxide. This last-mentioned salt constitutes 54·66 p. c. of the recently prepared crystals; 60 p. c. of the crystals after efflorescence in the air; and 66·07 p. c. of the white powder dried at 27°. If the heat be too suddenly applied, sulphite of ammonia sublimes and the residual zinc-sulphate contains excess of oxide. The crystals are soluble in water.

	At.	*Effloresced above 27°.*	
NH^3	2	34·0	27·60
Zno, SO^3	1	80·2	65·10
HO	1	9·0	7·30
	1	123·2	100·00

	Effloresced at ordinary temperatures.			*Recent crystals.*		
	At.			At.		
NH^3	2	34·0	25·72	2	34·0	22·63
ZnO, SO^3	1	80·2	60·66	1	80·2	53·40
HO	2	18·0	13·62	4	36·0	23·97
		132·2	100·00		150·2	100·00

c. NH^3+ZnO, SO^3. 1. Deposited in the preparation of *b*, in flocculent granules resembling starch.—2. Obtained as a gummy mass by fusing *b* for a short time. In whichever way the compound is prepared, it contains 1 atom of water. When fused for a longer time, it gives off water, and when strongly heated, leaves 75·92 per cent. of monosulphate of zinc-oxide. Both in the hydrated and in the fused state, it is decomposed by contact with water, the compound *b* together with sulphate of ammonia dissolving in the water, and sexbasic sulphate of zinc-oxide (p. 22) being separated. (Kane, *Ann. Chim. Phys.* 72, 304.)

	Dehydrated.		*Starch or gum-like salt.*		
NH^3	17·0	17·49	NH^3	17·0	16·01
ZnO, SO^3	80·2	82·51	ZnO, SO^3	80·2	75·52
			HO	9·0	8·47
	97·2	100·00		106·2	100·00

N. Sulphate of Zinc-oxide and Ammonia.—*Zinco-ammonic Sulphate.* Transparent, colourless, hard, bitter-tasting crystals, having precisely the form of the double sulphate of magnesia and ammonia. (Mitscherlich.) According to Tassaert (*Ann. Chim. Phys.* 24, 100) they consist of octohedral segments.

				Tassaert.
NH^3	17·0	8·49		8·04
ZnO	40·2	20·08		19·74
$2SO^3$	80·0	39·96		39·90
7HO	63·0	31·47		30·90
FeO, *accidental*				1·42
$NH^4O, SO^3+ZnO, SO^3+6Aq$	200·2	100·00		100·00

O. Ammonio-iodide of Zinc.—*a.* 100 parts of zinc-iodide, exposed to a current of ammoniacal gas, absorb 26·923 per cent. (not quite 3 atoms) of ammonia, becoming very hot, swelling up, and crumbling to a white, loosely-coherent powder. Cold water decomposes it, giving off ammonia and separating zinc-oxide free from iodine; but a small portion of zinc likewise dissolves.—*b.* The solution of zinc-iodide in aqueous ammonia, when left to evaporate freely, yields anhydrous white crystals which have a strong lustre, are permanent in the air, and when heated in close vessels are resolved into ammonia which escapes as gas, and iodide of zinc which sublimes; cold water acts upon them just as upon salt *a*; they dissolve readily in acids. (Rammelsberg, *Pogg.* 48, 152.)

	a.		Rammelsberg.		*b.*	*Crystallized.*		Rammelsberg.
$3NH^3$	51·0	24·38	21·21		$2NH^3$	34·0	17·69	
Zn	32·2	15·39	78·29		Zn	32·2	16·75	16·66
I	126·0	60·23			I	126·0	65·56	
	209·2	100·00	100·00			192·2	100·00	

P. Iodide of Zinc and Ammonium.—An aqueous mixture of iodide of zinc and hydriodate of ammonia, evaporated over oil of vitriol in a receiver containing air, yields extremely deliquescent crystals. (Rammelsberg, *Pogg*, 43, 665.)

	Crystallized.			Rammelsberg.
NH^4	18·0		5·96	
Zn	32·2		10·65	10·269
2I	252·0		83·39	80·644
NH^4I, ZnI	302·2		100·00	

Q. Ammonio-iodate of Zinc-oxide.—Separates from a solution of zinc-iodate in ammonia, in rhombic crystals by spontaneous evaporation, and as a white powder on the addition of alcohol. The crystals, when exposed to the air, effloresce rapidly from loss of ammonia. When heated, they melt and leave oxide of zinc. They are decomposed by water. (Rammelsberg, *Pogg.* 43, 665.)

	Crystallized.			Rammelsberg.
$4NH^3$	68·0		9·90	10·64
3ZnO	120·6		17·57	18·03
$3IO^5$	498·0		72·53	71·33
$4NH^3 + 3(ZnO, IO^5)$	686·6		100·00	100·00

R. Ammonio-bromide of Zinc.—A concentrated aqueous solution of zinc-bromide, supersaturated with ammonia and evaporated, yields colourless octohedrons, which fuse and give off all their ammonia when heated; and when digested with water, especially with the aid of heat, are completely resolved into precipitated oxide of zinc, and a solution of hydrobromate of ammonia free from zinc. (Rammelsberg, *Pogg.* 55, 240.)

	Crystallized.			Rammelsberg.
NH^3	17·0		13·32	12·98
Zn	32·2		25·24	25·82
Br	78·4		61·44	59·87
$NH^3, ZnBr$	127·6		100·00	98·67

S. Ammonio-bromate of Zinc-oxide.—When ammonia is added to an aqueous solution of zinc-bromate till the precipitate first formed is re-dis-

solved, and the liquid evaporated [best under a bell-jar with hydrate of potash and quick-lime], small prismatic crystals are obtained. These crystals when heated, are decomposed with a hissing noise and a backward and forward motion, and give off bromine. With water they are converted into oxide of zinc and bromate of ammonia which dissolves. When exposed to the air, they attract moisture and turn yellow, evolving bromine and afterwards giving up bromide of zinc to the water. (Rammelsberg, *Pogg.* 52, 90.)

	Crystallized.				Rammelsberg.
NH^3	17·0	...	8·39	.....	8·52
ZnO	40·2	...	19·84	.....	19·41
BrO^5	118·4	...	58·44		
3HO	27·0	...	13·33		
$NH^3 + ZnO, BrO^5 + 3Aq.$	202·6	...	100·00		

T. Ammonio-chloride of Zinc.—*a.* $2NH^3,ZnCl$.—Formed by passing ammoniacal gas through a hot concentrated solution of zinc-chloride till the precipitate is re-dissolved—filtering quickly, in case any flocculent matter should remain undissolved—and leaving the solution to cool. The compound *a* then separates. The mother-liquor, when evaporated, yields crystals of the compound *b*.—*a* appears in small laminæ, having a pearly lustre and feeling like mica. At 149° it gives off all its water and half its ammonia, and leaves 77·22 per cent. of a white powder, consisting of $NH^3,ZnCl$. When more strongly heated, it leaves NH^3, 2Zn.Cl. (Kane, *Ann. Chim. Phys.* 72, 290.)

	Crystallized.				Kane.
$2NH^3$	34·0	...	30·74		
Zn	32·2	...	29·11		
Cl	35·4	...	32·01	.....	31·14
HO	9·0	...	8·14		
$2NH^3 + ZnCl + Aq.$	110·6	...	100·00	=	$NH^2,ZnCl + NH^3,HO$.

b. $NH^3,ZnCl$.—For the preparation, *vid. a.*—Square prisms having a glassy lustre. The compound fuses when heated, giving off its water and half its ammonia, and forming a transparent liquid composed of $NH^3,2ZnCl$, and amounting to 85·64 per cent. of the original substance. (Kane.)

	Crystallized.				Kane.
$2NH^3$	34·0	...	19·08		
2Zn	64·4	...	36·14	.....	35·61
2Cl	70·8	...	39·73	.....	39·47
HO	9·0	...	5·05		
$2NH^3 + 2ZnCl + Aq.$	178·2	...	100·00		

c. $NH^3,2ZnCl$.—When *a* or *b* is fused, this compound remains in the form of a clear, colourless or yellowish liquid which, on cooling, solidifies into an amber-yellow, gummy, very slightly crystalline mass. It boils at a heat near redness and sublimes undecomposed in amber-coloured drops. When heated with lime, it evolves a large quantity of ammonia. When treated with water, it is resolved into the compound *b*, which dissolves, and oxychloride of zinc, $ZnCl,6ZnO + 6Aq$ (p. 32), which remains undissolved. (Kane.) According to Grouvelle, chloride of zinc absorbs ammoniacal gas; according to Perzoz, the quantity absorbed is half an atom, and the absorption does not take place without the aid of heat.

NH^3	17·0	.....	11·17
2ZnCl	135·2	.....	88·83
NH^3, 2ZnCl	152·2	.....	100·00

U. Chloride of Zinc and Ammonium.—A solution of 1 part of zinc-oxide in strong hydrochloric acid mixed with 1 part of sal-ammoniac and evaporated—the acid, as it escapes, being replaced—yields on cooling, transparent and colourless rectangular prisms, truncated at the lateral edges and the corners, and having a sharp metallic taste. They are permanent in dry air, but deliquesce in moist air, and dissolve without decomposition in water. (Schindler, *Mag Pharm.* 36, 37.) When heated, they are resolved into sal-ammoniac which volatilizes, and chloride of zinc which remains behind. They dissolve into $\frac{2}{3}$ pt. of cold water, producing a great fall of temperature and in 0·28 pt. boiling water. (Golfier—Basseyre, *Ann. Chim. Phys.* 70, 344.)

	Crystallized.				Schindler.
NH^4Cl	53·4	...	41·08	.....	41·20
ZnCl	67·6	...	52·00	.....	52·09
HO	9·0	...	6·92	.....	6·71
NH^4Cl, ZnCl + Aq.	130·0	...	100·00	.....	100·00

Oxide of zinc dissolves in aqueous sal-ammoniac. (Thénard, *Scher. J.* 10, 428.) A solution of hydrated zinc-oxide in gently-warmed sal-ammoniac yields the above mentioned crystals on evaporation; but, if it be boiled, the ammonia escapes, and basic hydrochlorate of zinc-oxide *a* (page 31) is produced, from which the compound *b* is precipitated on cooling. (Schindler.)

When chloride of zinc is precipitated by an insufficient quantity of ammonia, a precipitate is formed, containing oxide of zinc 79·86; chloride of zinc 14·80; sal-ammoniac 2·37; a slight excess of ammonia produces a gelatinous precipitate which exhibits an alkaline reaction, even after long washing, and contains 2·42 per cent. of ammonia and 11·16 chlorine; the liquid filtered from it yields crystals of the double chloride of zinc and ammonium. (Bonnet, *Ann. Pharm.* 9, 170.)

¶ By mixing solutions of 1 pt. sal ammoniac and 2 pts. chloride of zinc, Hautz obtained a salt which separated in crystals belonging to the oblique prismatic system. The crystals were very soluble in water and showed a tendency to deliquesce when exposed to the air.

	Crystallized.				Hautz.
NH^4	18·0	...	7·95	.....	8·00
2Zn	66·4	....	29·17	.....	29·05
3Cl	106·2	...	46·95	.....	46·46
4HO	36·0	...	15·93	.....	16·26
NH^4Cl, 2ZnCl + 4Aq.	226·6	...	100·00	.....	99·77

(*Ann. Pharm.* 66, 287.) ¶

Zinc and Potassium.

A. Alloy of Zinc and Potassium.—Combination between these two metals takes place at high temperatures only.—The alloy is a brittle, granular mass, which fuses at a red heat.—It oxides in the air, and

decomposes water rapidly, especially when acids are present. (Gay-Lussac, and Thénard.)

B. ZINC-OXIDE WITH POTASH.—Zinc dissolves in aqueous solution of potash very slowly and with evolution of hydrogen (Bischof, *Kastn. Arch.* 1, 193); more quickly when in contact with platinum; most quickly in contact with iron. (Runge, *Pogg.* 16, 129.) The ignited oxide dissolves with difficulty; the hydrate easily and abundantly.—The concentrated solution, when covered with a layer of alcohol, deposits small shining crystals, containing 1 At. zinc-oxide with 1 At. potash. They dissolve readily in water, and the solution, when boiled, deposits a white powder containing 2 At. zinc-oxide to 1 At. potash. (Laux, *Ann. Pharm.* 9, 183.) By the addition of a small quantity of alcohol, Frémy (*Compt. rend.* 15, 1106) obtained long needles containing 2 At. zinc-oxide with 1 At. potash; these, when treated with water, were immediately decomposed, yielding anhydrous zinc-oxide and aqueous solution of potash.—The solution of zinc-oxide in aqueous potash leaves on evaporation a white shining mass which becomes moist by exposure to the air. (Berzelius.)—2 parts of hydrated zinc-oxide dissolve in 5 parts of potash-ley of 1·3 specific gravity. When the solution is evaporated to dryness and the residue fused, an enamel-like mass is formed, from which water extracts the potash; the solution mixed with eight times its volume of alcohol deposits nearly the whole of the zinc-oxide. (Bonnet.)—The solution of zinc-oxide in caustic potash is rendered turbid only by a very large quantity of water.

When a solution of zinc-vitriol is mixed with a quantity of potash sufficient to re-dissolve the precipitate, and then exposed to the air for some time, a precipitate is formed containing zinc-oxide, potash, and carbonic acid, but no sulphuric acid. The mixture yields no deposit, when boiled out of contact of air; but when it is boiled in an open vessel, or if it has been exposed to the air before boiling, it yields a powder which becomes very heavy when dry and consists of pure hydrated oxide of zinc. If the potash contains silica, silicate of zinc-oxide and potash is formed on boiling. The precipitate which Vauquelin & Buchner (*Repert.* 14, 381) obtained by boiling a solution of potash saturated with zinc-oxide, and which, according to their statement, consists of zinc-oxide mixed with a small quantity of potash, is likewise regarded by Schindler as silicate of zinc-oxide and potash. Water added to the mixture throws down a large quantity of zinc-oxide containing potash, sulphuric acid, and water; a larger quantity of water precipitates the pure hydrated oxide. (Schindler.)—Zinc-oxide boiled with aqueous carbonate of potash extracts potash from that compound, and afterwards exhibits an alkaline reaction on turmeric paper; the potash may be removed from it by long washing with water. (Wackenroder.)

C. CARBONATE OF ZINC-OXIDE AND POTASH.—*Zinco-potassic Carbonate.*—A zinc-salt precipitated by excess of carbonate of potash at ordinary temperatures, yields a stiff, gelatinous precipitate, which cakes together in drying, and consists of a mixture of $\frac{2}{3}$-carbonate of zinc-oxide (p. 12) and double carbonate of zinc-oxide and potash. Gives off all its carbonic acid when ignited. (Schindler, *Mag. Pharm.* 36, 56.)

D. SULPHATE OF ZINC-OXIDE AND POTASH.—*Zinco-potassic Sulphate.*—Crystallizes in the same form as sulphate of magnesia and ammonia. (Mitscherlich.) *Fig.* 84; $y : u = 102° 20'$; $u' : u = 108° 40'$. (Teschemacher,

Kastn. Arch. 13, 197.) Sp. gr. 2.153. (Kapp.) The crystals have an acid reaction. In vacuo, they give off 5 atoms of water at 25·5°, but the sixth they retain till heated to 121°. (Graham.) Soluble in 5 parts of cold water. (Bucholz. Junr. *N. Tr.* 9, 2, 26.)

	Crystallized.				Bucholz.
KO	47·2	....	21·32	.....	18·2
ZnO	40·2	....	18·16	.....	21·4
$2SO^3$	80·0	....	36·13	.....	36·2
6HO	54·0	....	24·39	.....	24·5
$KO,SO^3 + ZnO,SO^3 + 6Aq.$	221·4	....	100·00	.....	100·3

E. Iodide of Zinc and Potassium.—*Zinco-potassic Iodide.*—A solution of iodide of zinc and iodide of potassium evaporated over oil of vitriol under a receiver containing air, yields very deliquescent crystals. (Rammelsberg, *Pogg.* 43, 665.)

					Rammelsberg.		Or:		
K	39·2	....	8·14	.....	8·92	KI	165·2	....	34·4
2Zn	64·4	....	13·37	.....	12·95	2ZnI	316·4	....	65·6
3I	378·0	....	78·49	.....					
KI,2ZnI	481·6	....	100·00	.....			481·6	....	100·0

F. Chloride of Zinc and Potassium.—*Zinco-potassic Chloride.*—The preparation, crystalline form, and other properties of this compound are precisely similar to those of the chloride of zinc and ammonium; but it deliquesces more rapidly. (Schindler.)

G. Fluoride of Zinc and Potassium.—*Zinco-potassic Fluoride.*—KF,ZnF.—Colourless, crystalline granules, soluble in water. (Berzelius.)

On the properties of crystals obtained by supersaturating nitrate of zinc with iodide of potassium, and containing nitric acid, *vid.* Anthon, *Repert.* 51, 115.

Zinc and Sodium.

A. Alloy of Zinc and Sodium.—Four volumes of zinc-filings unite with 1 volume of sodium at a dull red heat, and form a bluish-grey, brittle alloy which has a finely laminar texture, oxidates slowly in the air, and effervesces slightly with water, but strongly with aqueous acids. (Gay-Lussac and Thénard.)

B. Zinc-oxide with Soda.—Hydrated zinc-oxide dissolves readily in aqueous solution of soda; metallic zinc only when heat is applied; it then dissolves with evolution of hydrogen. (Lassonne.) The solution, when exposed to the air, deposits small shining crystals of hydrated obasic zinc-carbonate. (Wöhler.) Zinc-oxide boiled with solution of carbonate of soda extracts from it only a trace of soda; if sulphate of soda is mixed with the solution, the zinc-oxide extracts from it both soda and sulphuric acid, which it retains with great obstinacy. (Wackenroder.)

C. Carbonate of Zinc-oxide and Soda.—*Zinco-sodic Carbonate.*—Zinc dissolves slowly in aqueous carbonate of soda, with evolution of hydrogen. The solution, set aside for a few days, deposits small, colourless, strongly lustrous, hard, regular tetrahedrons and octahedrons, having their edges and solid angles truncated. They become opaque when

heated, and turn yellow on ignition; and if afterwards treated with water, they yield a solution of carbonate of soda and a residue of pure oxide of zinc. (Wöhler, *Pogg.* 28, 616.) Oxide of zinc does not dissolve in carbonate of soda fused before the blowpipe.

B. Zinc-oxide dissolves in *Borax* and in *Microcosmic* salt, yielding a clear glass which becomes milk-white on gentle flaming, and if the zinc-oxide is in excess, becomes enamel-white on cooling.

E. SULPHATE OF ZINC-OXIDE AND SODA.—*Zinco-sodic Sulphate.*—Separates from a solution of zinc-vitriol and bisulphate of soda, when evaporated in vacuo over oil of vitriol. (Graham.) According to Graham, monosulphate of soda and zinc-vitriol, mixed in any proportions whatever, do not yield this double salt, but each salt crystallizes out by itself. Karsten, on the other hand (*Schrift d. Berl. Akad.* 1841), obtained crystals of the double salt, both by mixing Glauber's salt with a saturated solution of zinc-vitriol, and setting the mixture aside for a few days, and likewise by dissolving zinc-vitriol at ordinary temperatures in a saturated solution of Glauber's salt, and leaving the mixture to evaporate either spontaneously or with the aid of heat; it was only when the mixture was strongly heated and then suddenly cooled, that the two salts crystallized out separately. Karsten likewise obtained the double salt with common salt and zinc-vitriol.

The dehydrated salt melts without decomposition at an incipient red-heat, and on cooling, solidifies in a white, opaque mass. The salt crystallizes in tables contains 4 atoms of water; it deliquesces only in moist air, and when dissolved in water, separates into the two simple salts. (Graham, *Phil. Mag. J.* 18, 417.)

F. IODIDE OF ZINC AND SODIUM.—*Zinco-sodic Iodide.*—Preparation and properties, similar to those of the potassium-salt. (Rammelsberg.)

	Crystallized.			Rammelsberg.
Na	23·2	....	6·94	6·95
Zn	32·2	....	9·62	9·41
2I	252·0	....	75·36	74·85
3HO	27·0	....	8·08	
NaI, ZnI + 3Aq.	334·4	....	100·00	

G. CHLORIDE OF ZINC AND SODIUM.—*Zinco-sodic Chloride.*—An aqueous solution of common salt and zinc-chloride quickly evaporated yields six-sided laminæ, having a sharp taste, and easily soluble. If the solution be slowly evaporated, the chloride of sodium crystallizes out alone. (Schindler, *Mag. Pharm.* 36, 48.)

ZINC AND BARIUM.

IODIDE OF ZINC AND BARIUM.—*Zinco-barytic Iodide.*—Preparation and properties similar to those of the potassium-salt.

	Crystallized.			Rammelsberg.
Ba	68·6	....	13·42	11·71
2Zn	64·4	....	12·60	12·80
3I	378·0	....	73·98	
BaI, 2ZnI	511·0	....	100·00	

Baryta, strontia, and lime dissolved in water, and mixed with the compound of zinc-oxide and ammonia, deprive that compound of part of its zinc-oxide, and are precipitated in combination with that oxide. (Berzelius.)

Zinc and Magnesium.

Sulphate of Zinc-oxide and Magnesia.—*Zinco-magnesic Sulphate.*—Sulphate of magnesia dissolves in a cold saturated solution of zinc-vitriol forming a clear liquid at first; but after awhile, the double salt is deposited. (Karsten.)

Zinc and Aluminum.

A. Aluminate of Zinc-oxide.—*a. Gahnite.*—Regular octohedrons; sp. gr. 4·23. Harder than quartz; translucent, green; yields a pale bluish-green powder. Does not fuse before the blowpipe; bakes together with carbonate of soda without dissolving in it, and forms a dark-coloured slag, which, when finely pulverized, forms a deposit of zinc-oxide upon the charcoal; dissolves sparingly and with great difficulty in borax or in microcosmic salt; dissolves in a mixture of borax and carbonate of soda, forming a clear glass coloured by iron. (Berzelius.) Insoluble in aqueous acids and alkalis.

	Gahnite.				Abich. Fahlun.		Abich. America.
MgO					5·25		2·22
ZnO	40·2		43·9		30·02		34·80
FeO					5·85		4·55
Al^2O^3	51·4		56·1		55·14		57·09
SiO^2					3·84		1·22
ZnO,Al^2O^3	91·6		100·0		100·10		99·88

Part of the ZnO is replaced by MgO and FeO.

b. Hydrate of alumina abstracts the zinc-oxide from the aqueous solution of the compound of zinc oxide and ammonia; aluminate of zinc-oxide is likewise precipitated on mixing the compound of zinc-oxide and ammonia with a saturated solution of hydrate of alumina in potash. This compound is soluble in potash. (Berzelius.) The compound of zinc-oxide and potash likewise forms, with aluminate of potash, a precipitate soluble in excess of potash. (Sander, *Ann. Pharm.* 9, 181.)

B. Sulphate of Alumina and Zinc-oxide.—*Zinc-alum*$=ZnO,SO^3+Al^2O^3,3SO^3+24Aq$. (Kane.)

C. Fluoride of Aluminum and Zinc.—ZnF,Al^2F^3.—Formed by evaporating the aqueous solution of hydrofluate of zinc-oxide and hydrofluate of alumina. Long, colourless needles, slowly but completely soluble in water. Ammonia added to the solution throws down aluminate of zinc-oxide. (Berzelius.)

Zinc and Silicium.

A. Silicate of Zinc-oxide.—*Zinc-glance* or *Siliceous Calamine* occurs in transparent and colourless crystals belonging to the right

prismatic system. Right rhombic prisms, having the obtuse (rarely also the acute) lateral edges replaced by planes, with two bevelling surfaces resting sometimes on the two acute, sometimes on the two obtuse lateral edges. Cleavage parallel to *u* and *p*. Sp. gr. 3·38. Harder than felspar. —Decrepitates slightly when heated, losing water and becoming opaque; does not fuse before the blowpipe, but swells up when strongly ignited; intumesces slightly with carbonate of soda but does not dissolve in it, and gives, though not readily, a deposit of zinc-oxide. In borax or microcosmic salt, it fuses to a transparent glass, which, however, becomes turbid on cooling. With nitrate of cobalt it assumes a green colour when gently heated, light-blue on the edges when more strongly ignited. (Berzelius.) Dissolves readily in acids, with separation of a siliceous jelly; dissolves for the most part in caustic potash.

			Berzelius. Limburg.	Berthier. Breisgau.	Smithson. Retzbanya.
2ZnO	80·4	66·78	66·37	64·5	68·3
SiO^2	31·0	25·75	26·23	25·5	25·0
HO	9·0	7·47	7·40	10·0	4·4
$2ZnO,SiO^2+Aq.$	120·4	100·00	100·00	100·0	97·7

The same compound occurs in the anhydrous state but impure, as *Williamsite* or *Hebetine*.

B. Hydrated Fluoride of Silicium and Zinc, or Hydrofluate of Silica and Zinc-oxide.—A solution of zinc-oxide in hydrofluosilicic acid yields, when evaporated at a high temperature, three and six-sided, transparent, colourless prisms, permanent in the air, and very easily soluble in water; ZnF,SiF^2+7Aq. (Berzelius.)

C. Silicate of Zinc-oxide and Potash.—Separates in white flakes when zinc in contact with iron is dissolved in potash-ley containing silica. The flakes contain water; they dissolve in excess of caustic potash, and likewise, with separation of a jelly, in acids. (Schindler.)

Zinc and Tungsten.

A. Tungstate of Zinc-oxide.—White powder, insoluble in water.

B. Sulphotungstate of Zinc.—ZnS, WS^3. The mixture of an aqueous zinc-salt with sulphotungstate of potassium gives after 24 hours, a pale yellow, pulverulent precipitate. (Berzelius.)

Zinc and Molybdenum.

A. Molybdate of Zinc-oxide.—Formed by precipitating a zinc-salt with molybdate of ammonia. Yellowish-white powder, sparingly soluble in water, more easily soluble in acids, and containing, according to Brandes, 36·25 zinc-oxide and 63·75 molybdic acid.

B. Sulphomolybdate of Zinc.—Dark brown precipitate, insoluble in water. (Berzelius.)

C. Persulphomolybdate of Zinc.—Red precipitate. (Berzelius.)

D and E. MOLYBDATE OF ZINC-OXIDE AND AMMONIA, and MOLYBDATE OF ZINC-OXIDE AND POTASH.—Both these double salts are soluble in water. (Berzelius.)

ZINC AND VANADIUM.

VANADIATE OF ZINC-OXIDE.—*a. Monovanadiate.*—By double decomposition. White precipitate, insoluble in water, even at a boiling heat. *b. Bivanadiate.*—Transparent, orange-yellow crystals, soluble in water. (Berzelius.)

ZINC AND CHROMIUM.

CHROMATE OF ZINC-OXIDE.—*a. Dichromate.*—The yellow precipitate which monochromate of potash produces in a solution of zinc-vitriol. (Thomson, *Phil. Mag. Ann.* 3, 81.) When the chromate of potash is dropt into a boiling solution of zinc-vitriol, the precipitate formed has a peculiarly fine yellow colour. (Bensch.) The supernatant liquid remains yellow even when the zinc-salt is in excess. [It probably contains bichromate of potash.] Zinc-salts are not precipitated by bichromate of potash. (Wöhler.)

b. Monochromate.—A solution of zinc-carbonate in aqueous chromic acid yields transparent, topaz-yellow crystals, having the form of zinc-vitriol and a specific gravity of 2·096 at 15°. The crystals are easily soluble in water, and when heated, dissolve in their water of crystallization; the dehydrated salt is strongly heated by contact with water. (Kopp, *Ann. Pharm.* 42, 98.)

					Kopp.
ZnO, CrO^3	92·2	....	59·41	.....	57·8
7HO	63·0	....	40·59	.....	42·2
$ZnO, CrO^3 + 7Aq$....	155·2	....	100·00	.....	100·0

¶ By subsequent examination, Kopp has discovered that the crystals which he originally took for pure chromate of zinc-oxide, really consisted of ordinary zinc-sulphate containing small quantities of zinc-chromate intimately bound up with them: the crystals when dissolved in water gave the reactions of chromic acid, but contained only 3·5 per cent. of that acid, instead of 33·6 as required by the formula, $ZnO, CrO^3 + 7Aq$. The formation of the zinc-sulphate is due to the presence of sulphuric acid in the chromic acid used in the preparation. (*Ann. Pharm.* 57, 386.) ¶

B. CHROMATE OF ZINC-OXIDE AND POTASH.—*Zinco-potassic Chromate.* If the yellow flocculent precipitate obtained by mixing zinc-vitriol with monochromate of potash be left immersed in the liquid for 24 hours, it changes to an orange-yellow powder, which is a compound of chromate of potash with chromate of zinc-oxide. It loses by ignition 15 per cent. of oxygen and water, and leaves a dark brown powder from which water extracts a quantity of monochromate of potash amounting to 21 per cent. of the double salt, and leaves violet-brown *Chromite of Zinc-oxide*, which dissolves in oil of vitriol, forming a dark-green solution. The double salt is slightly soluble in cold water and imparts a yellow colour to large quantities of it; in boiling water it forms a deep yellow solution, with separation of a lighter-coloured salt, probably basic. (Wöhler, *Berzelius Lehrb.* 4, 487.)

Zinc and Uranium.

Uranate of Zinc-oxide.—1. By precipitating zinco-uranic acetate with baryta-water.—2. When uranic nitrate is precipitated by zinc, the zinc becomes covered with a solid yellow film of uranate of zinc-oxide, which prevents further combination. (Wertheim, *J. pr. Chem.* 29, 227.)

Zinc and Manganese.

Permanganate of Zinc-oxide.—Deliquescent. (Mitscherlich.)

Zinc and Arsenic.

A. Arsenide of Zinc.—*a.* When 75·2 parts (1 At.) of arsenic-powder is brought in contact with 128·8 parts (4 At.) of zinc fused but not red-hot, combination takes place, the whole mass glowing vividly with a dark red light, and some of the arsenic volatilizing. (A. Vogel.) *b.* With 64·2 parts (2 At.) zinc and 75·2 parts (1 At.) arsenic similarly treated, the ignition is less vivid, because the resulting compound is less fusible and solidifies more quickly. This compound, when treated with hydrochloric acid, gives off pure arseniuretted hydrogen, without any admixture of free hydrogen. (A. Vogel, *J. pr. Chem.* 6, 345.) 100 parts of zinc-turnings heated with 100 parts of arsenic-powder combine without ignition and yield 172 parts of a very brittle alloy. (Gehlen.) Equal parts of granulated zinc and pulverized arsenic heated in an earthen retort at a gradually increasing temperature, yield a well-fused, grey, brittle alloy, having a fine-grained fracture; this alloy, when dissolved in dilute sulphuric acid, evolves pure arseniuretted hydrogen gas, and leaves a grey metallic powder which contains excess of arsenic, gives off that excess when heated, and is thereby rendered soluble in acids. (Soubeiran.) Arsenide of zinc is likewise obtained by heating zinc with arsenious acid, (Bergman.) With 2 parts of zinc-cuttings and 1 part of arsenious acid, the reaction takes place with combustion and explosion. (Gehlen.)

B. Arseniate of Zinc-oxide or Zinc-arseniate.—*Tris-arseniate.* When di-arseniate of ammonia, potash, or soda is mixed with a zinc-salt, the liquid turns sour, and tris-arseniate of zinc-oxide is precipitated. (Mitscherlich.) The precipitate formed by arsenic acid in a solution of zinc-acetate is either the same salt, or a di-arseniate. White powder, insoluble in water, but soluble in arsenic and nitric acid. Hydrogen gas passed over the ignited salt, decomposes it, according to Soubeiran, into water, arsenic, and zinc-oxide, the latter remaining behind.

b. Acid Salt. Formed by dissolving zinc, the oxide, or the salt *a* in arsenic acid. When metallic zinc is used, arseniuretted hydrogen is given off, and solid arsenide of hydrogen separates in the form of a brown powder. The acid solution yields cubes on evaporation. (Berzelius.) When completely saturated with zinc, it solidifies to a transparent jelly. (Fischer, *Pogg.* 9, 261.)

C. Hyposulpharsenite of Zinc.—Yellowish red. (Berzelius.)

D. Sulpharsenite of Zinc.—Hydrosulphate of soda saturated with arsenious sulphide, forms, with neutral zinc-salts, a bulky, lemon-yellow

precipitate which becomes orange-yellow on drying. This, when gently heated, gives off part of the arsenious sulphide, and leaves a hard, yellow, agglomerated compound of zinc-sulphide with a small quantity of arsenious sulphide; the latter is completely driven off at the melting point of glass. (Berzelius, *Pogg.* 7, 145.)

E. Sulpharseniate of Zinc.—*a. Terbasic salt.*—$3ZnS,AsS^3$.—By precipitating a zinc-salt with trisulpharseniate of sodium. Pale yellow flakes, which, when dry, yield an orange-yellow powder.—*b. Bibasic.* $2ZnS, AsS^5$. By precipitating with disulpharseniate of sodium. Forms somewhat brighter yellow flakes, but exhibits the same colour as *a* when dry. (Berzelius.)—*c. Monobasic.*—When zinc-oxide and arsenic acid are dissolved together, even in a very large excess of hydrochloric or sulphuric acid, sulphuretted hydrogen precipitates the whole of the zinc [provided the quantity of arsenic acid is sufficient] in the form of yellow ZnS, AsS^5. But if the arsenic acid be previously reduced to the state of arsenious acid by the action of sulphurous acid, sulphuretted hydrogen precipitates only tersulphide of arsenic, and leaves all the zinc in solution. (Wöhler, *Jahresb.* 21, 2, 150.)

F. Arseniate of Zinc-oxide with Ammonia.—Formed by mixing hydrochlorate of zinc-oxide with a quantity of sal-ammoniac sufficient to prevent precipitation by ammonia, and then digesting the solution with a mixture of ammonia and arseniate of potash. The precipitate, which is flocculent at first and afterwards becomes crystalline, forms, after pressure between paper and drying, a white powder, soluble in acids, ammonia, and potash, but not in water. At 100° it gives off the greater part of its water with a portion of ammonia, and on ignition leaves a residue amounting to 84·33 per cent., and consisting of 43·57 zinc-oxide with 40·76 arsenious acid. (Bette, *Ann. Pharm.* 15, 141.)

			Bette.
NH^3	17·0	6·08	5·97
$3ZnO$	120·6	43·13	43·57
AsO^5	115·0	41·13	40·76
$3HO$	27·0	9·66	9·70
$NH^3+3ZnO,AsO^5+3Aq.$	279·6	100·00	100·00

Zinc and Antimony.

A. Antimonide of Zinc.—These two metals fuse together with facility—and, according to Gehlen and A. Vogel, without emission of light—and form a hard, brittle, steel-coloured alloy, whose density is less than the medium density of its elements. (Gellert.)

B. Antimoniate of Zinc-oxide.—The precipitate formed in a solution of zinc-vitriol by a small quantity of antimoniate of potash disappears again, and does not become permanent till a larger quantity of antimoniate of potash is added; white crystalline grains are then deposited, in the course of a few hours, on the sides of the vessel. The salt when heated, gives off all its water and turns yellow, but without any appearance of luminosity. It does not fuse before the blowpipe on charcoal and can only be reduced by addition of an alkali; it is very slightly soluble in water. (Berzelius.)

C. SULPHANTIMONIATE OF ZINC.—$3ZnS,SbS^5$. Zinc-vitriol dropt into excess of aqueous sulphantimoniate of sodium, forms a deep orange-yellow precipitate, which dissolves in the liquid on boiling, and passes through the filter during washing. If the zinc-sulphate be added in excess and the liquid boiled for a short time, a deep orange-yellow precipitate is formed, which dries up to a brown-red mass having a shining fracture. This substance, when ignited in a retort, yields sulphurous acid and sulphur, and leaves a half-fused residue amounting to 82·9 per cent. It dissolves in boiling hydrochloric acid. In caustic potash it dissolves with separation of zinc-sulphide, and forms a yellow solution, from which acids precipitate pentasulphide of antimony, with slight evolution of sulphuretted hydrogen. (Rammelsberg, *Pogg.* 52, 223.)

				Rammelsberg.
4Zn	128·8	....	32·71	30·85
8Sb	129·0	....	32·76	30·81
8S	128·0	....	32·50	33·17
O	8·0	....	2·03	
$3ZnS, SbS^5 + ZnO$	393·8	....	100·00	

ZINC AND TELLURIUM.

A. TELLURIDE OF ZINC.—These metals when heated unite with great evolution of heat, and form a grey, porous, difficultly soluble alloy, having a metallic lustre and crystalline fracture, insoluble in strong sulphuric or hydrochloric acid. (Berzelius, *Lehrb.* 3, 384.)

B. TELLURITE OF ZINC-OXIDE.—By double decomposition. White flakes. (Berzelius.)

C. SULPHOTELLURITE OF ZINC.—$3ZnS,TeS^2$.—By double decomposition. The precipitate, which is light-yellow at first, gradually turns brown. (Berzelius.)

ZINC AND BISMUTH.

Alloy of Zinc and Bismuth?—The two metals will not unite by fusion. (Cramer.) On melting them together in equal parts, two layers are formed, the upper consisting of zinc, the lower of bismuth containing a small quantity of zinc, and therefore of a lighter red; finer-grained and more brittle than pure bismuth, but expanding with equal force as it solidifies. (Marx, *Schw.* 58, 465.) By fusing together 16·12 pts. (6 At.) zinc and 17·73 pts. (1 At.) bismuth, an upper layer is formed, consisting of zinc and amounting to 13·40 parts, and a lower layer, amounting to 19·40 parts and consisting of bismuth, which, where it borders on the zinc, is somewhat more laminar, in consequence of admixture of zinc; but no chemical compound is obtained. (Fournet, *Ann. Chim. Phys.* 24, 247.)

OTHER COMPOUNDS OF ZINC.

With Tin, Lead, Iron, Cobalt, Nickel, Copper, Mercury, Silver, Gold, Platinum, and Palladium. Very small quantities of tin, lead, iron, copper, or mercury, diminish the solidity of zinc; a very small quantity of iron or copper accelerates its solution in acids; a very small quantity of lead or mercury, especially the latter, retards the solution. (Karsten, *J. pr. Chem.* 16, 380.)

Chapter XXIX.

CADMIUM.

Stromeyer. *Schw.* 22. 262: abstr. *Gilb.* 60. 193.
Hermann. *Gilb.* 59. 95 and 113: 66. 276.
Meissner. *Gilb.* 59. 83.
Roloff. *Berl. Jahrb.* 1819. 250: *Gilb.* 70. 194.
Karsten. *Archiv f. Bergbau und Hüttenwesen*, 1, 209; abstr. *Berl. Jahrb.* 1819. 244.
John. *Handbuch der Chemie.* 3. 299; also *Berl. Jahrb.* 1819, 243.—Further: *Berl. Jahrb.* 1820. 365.
Children. *Phil. Mag.* No. 259. 63: also *Schw.* 24. 441.
Clarke. *Ann. Phil.* 15. 272: also *Schw.* 30. 222.—Further: *Ann. Phil.* 18. 123: 8. 195.
Herapath. *Ann. Phil.* 19. 435.

Synonymes. *Klaprothium. Melinum.*

History. Cadmium appears to have been discovered about the same time—in the spring of 1818—by Stromeyer and by Hermann; the more accurate investigation of it is, however, due to Stromeyer.

Sources. As sulphide of cadmium:—also in small quantity in several varieties of Calamine and Blende, namely, in the radiated Blende of Przibram, to the amount of 2 or 3 per cent. (Stromeyer.) In the Blende of Nuissière to the amount of 1·136 per cent. (Damour, *J. pr. Chem.* 13, 334.) In silicate of zinc from Freiberg and from Derbyshire; in carbonate of zinc from Mendip; in carbonate and silicate of zinc from the Cumberland mines; in commercial English zinc: but not in the carbonate of zinc from Holywell, or in the silicate from Hungary. (Clarke.) The flowers of zinc obtained in the preparation of zinc from calamine in Silesia (p. 1) likewise contain about 3 per cent. of cadmium. All these bodies, when heated in the inner blowpipe-flame, form a red deposit on charcoal or on platinum.

Preparation. 1. Cadmiferous zinc, oxide of zinc, or zinc ore, is dissolved in dilute sulphuric acid; the solution supersaturated with acid; the cadmium precipitated by sulphuretted hydrogen; the sulphide of cadmium washed and dissolved in strong hydrochloric acid; the excess of that acid expelled by evaporation; and the cadmium precipitated as a carbonate by means of carbonate of ammonia, which is added in slight excess, in order to re-dissolve any copper or zinc that may be mixed with the cadmium. The oxide of cadmium, after being washed and then heated to redness to free it from carbonic acid, is mixed with thoroughly ignited

lamp-black, and heated to redness in glass or earthen retorts: the metal then distils over. (Stromeyer.)—John treats the cadmiferous zinc with a quantity of dilute sulphuric acid, not sufficient to dissolve it,—whereupon the dissolved cadmium is precipitated by the excess of zinc in grey flakes. These flakes are dissolved in dilute sulphuric acid—the solution evaporated to dryness—the residue dissolved in water—the solution acidulated with hydrochloric acid—and the cadmium precipitated from it by zinc.—3. John treats the solution of cadmiferous zinc-flowers in sulphuric acid with sulphuretted hydrogen, in order to precipitate the cadmium in the form of sulphide—decomposes the precipitate with nitric acid—evaporates—dissolves the residue in dilute hydrochloric acid—and precipitates the cadmium by zinc.—4. In the distillation of zinc in England, the cadmium-vapours, being the more volatile, pass over before the zinc-vapours, and burn with a brown flame, forming a yellow, brown, or black oxide, which, besides sulphide of cadmium, oxide of zinc, and carbon, contains about 20 per cent. of cadmic oxide, and consequently, when dissolved in hydrochloric acid and precipitated by zinc, yields a large quantity of cadmium, which may be purified by sublimation. (Herapath.)—5. In Silesia, cadmium is prepared on the large scale from flowers of zinc, by gently igniting them with charcoal powder in earthen tubes—collecting the metallic powder deposited in the receiver [still containing zinc to the amount of half its weight] and distilling it twice in the same apparatus—and finally fusing the sublimed metal in a crucible with tallow. (Hollunder, *Kastn. Arch.* 12, 245.) It is not easy to get rid of all the zinc by this process.

Properties. Crystallizes readily in octohedrons; has a dense texture and indented fracture. Soft, but harder and more coherent than tin; easily cut with the knife; very flexible; very easily beaten out into thin plates or drawn into wires. (Stromeyer.) When bent, it emits a crackling noise like tin. Specific gravity after fusion, 8·604 (Stromeyer), 8·6355 (Karsten), 8·67 (Children), 8·677 (Herapath), 8·75 (John); after hammering, 8·6944 (Stromeyer), 9·05 (Children). Has a strong lustre. In colour it is intermediate between tin and zinc. Fuses below a red heat; volatilizes somewhat below the boiling point of mercury, and without emitting any particular odour. (Stromeyer.)

Compounds of Cadmium.

Cadmium and Oxygen.

A. *Suboxide of Cadmium ?*

Oxalate of cadmic oxide, heated in a retort to the melting point of lead, gives off water, carbonic acid, and marsh-gas, and is converted into a green powder. Mercury does not extract any metal from this powder. When heated in the air, it glows vividly, gives off a cloud of brown oxide, and leaves a mixture of metal and oxide, which partly fuses together in the form of golden-yellow grains of oxide mixed with metal. When treated with dilute sulphuric acid, it effervesces slightly from the escape of carbonic acid still retained in it, and yields cadmic oxide to the acid, while metallic cadmium remains behind. By dissolving it in nitric acid, evaporating to dryness, and igniting, 106·13 parts of cadmic oxide

are obtained: hence it contains 93·3 [92·9] per cent. of metal and 6·7 [7.1] of oxygen. (Marchand, *Pogg.* 38, 145.) Its composition is therefore nearly Cd^2O.

B. Cadmic Oxide.

Protoxide of Cadmium. Kadmiumoxyd, Oxyde cadmique.

Cadmium becomes somewhat tarnished by exposure to the air. (Stromeyer.) In moist air free from carbonic acid, it remains unchanged. When immersed in water and exposed to air free from carbonic acid, it becomes covered with a white powder, probably consisting of hydrated oxide; in air containing carbonic acid, it acquires a whitish-grey deposit, which contains carbonic acid. (Bonsdorff, *Pogg.* 42, 336.) When exposed to the air under water containing $\frac{1}{300}$ of potash hydrate, the metal becomes blackish-grey, but yellow after drying, and a trace of cadmic oxide dissolves in the water. (A. Vogel, *J. pr. Chem.* 14, 107.) The metal burns easily when heated in the air, forming cadmic oxide, which rises in the form of a brownish-yellow, inodorous cloud. (Stromeyer.) At ordinary temperatures it does not decompose water, unless one of the stronger acids, such as sulphuric, hydrochloric, or acetic acid is present, the decomposition then taking place with slow evolution of hydrogen gas. (Stromeyer.) Cadmium decomposes vapour of water at temperatures above the boiling point—as when a mixture of aqueous vapour and cadmium vapour is passed through a red-hot tube—the products being cadmic oxide and hydrogen gas. (Regnault, *Ann. Chim. Phys.* 62, 351.) It oxidizes and dissolves rapidly in cold nitric acid. (Stromeyer.) Cadmic oxide is obtained by burning cadmium, or by igniting the carbonate or nitrate.

Cadmic oxide is a powder, sometimes of a brownish-yellow, sometimes of a brownish red, and sometimes of a dark brown colour. Does not fuse, or volatilize, or decompose, even at the most intense white heat. (Stromeyer.) Specific gravity 6·9302. (Karsten.) Herapath, on subliming the metal in a glass tube containing air, obtained the oxide in purple, opaque needles, aggregated in stellate masses.

				Stromeyer.		John.
Cd	56	87·5	.....	87·45	.....	90 — 91
O	8	12·5	.....	12·55	.....	10 — 9
CdO	64	100·0	.....	100·00	.....	100 — 100

CdO 696·77 + 100 = 796·77. (Berzelius.)

Charcoal withdraws oxygen from cadmic oxide at a low red heat. The cadmium, as it is reduced on charcoal before the blowpipe, is immediately burnt again, and produces a brownish yellow or a red film upon the charcoal.

Combinations. a. With water.—Hydrate of Cadmic Oxide.—Formed by precipitating a cadmic salt in solution by caustic potash. ¶ If the solution be concentrated, a basic salt is obtained; but from a dilute solution, the hydrated oxide CdO,HO is obtained. (Schaffner, *Ann. Pharm.* 51, 173.) ¶ White; loses its water at a red heat; absorbs carbonic acid from the air. ¶ Nicklès has obtained the hydrated oxide in the crystalline state by the action of aqueous ammonia on metallic cadmium placed in contact with iron. The compound thus formed had nearly the composition CdO,HO. (*J. Pharm.* [3], 12, 61.) ¶

b. With Acids, forming the SALTS OF CADMIC OXIDE, or CADMIC SALTS. —These salts are mostly colourless; those which are soluble in water, redden litmus; they have a disagreeable metallic taste, and act as emetics. They give off their acid by ignition, provided the acid is volatile. When heated with carbonate of soda on charcoal in the inner blowpipe-flame, they form a yellow or brown-red deposit on the charcoal. The solutions of these salts give the following reactions: Zinc throws down metallic cadmium in dendrites. Clarke's statement that cadmium is likewise precipitated by iron, is contradicted by Meissner and Fischer.—Sulphuretted hydrogen passed through cadmic solutions, even when a large excess of acid is present, precipitates the whole of the cadmium in the form of sulphide, which has a lemon-yellow colour at first, but afterwards becomes orange-yellow. A similar effect is produced by alkaline hydrosulphates, the precipitate being insoluble in excess. The hydrated sulphides of manganese, iron, cobalt, and nickel, when recently precipitated, likewise throw down sulphide of cadmium from cadmic salts. (Anthon. *J. pr. Chem.* 10, 353.)—Caustic alkalis throw down white hydrate of cadmic oxide, very easily soluble in a slight excess of ammonia, but insoluble in potash or soda. Sulphuretted hydrogen likewise precipitates sulphide of cadmium from the solution in excess of ammonia.— The monocarbonates and bicarbonates of ammonia, potash, and soda, throw down white carbonate of cadmic oxide, insoluble in excess of the alkaline carbonates. If the salt contains a large quantity of free acid, the precipitate dissolves in excess of carbonate of ammonia, but not otherwise. (Stromeyer.)—Phosphate of soda throws down white phosphate of cadmic oxide.—Oxalic acid and alkaline oxalates precipitate white oxalate of cadmic oxide, insoluble in alkaline oxalates, but easily soluble in ammonia. The white precipitate produced by ferrocyanide of potassium, and the yellow precipitate produced by the ferricyanide, are soluble in hydrochloric acid.—The addition of hyposulphite of soda and hydrochloric acid does not produce a precipitate of sulphide of cadmium; neither is any precipitate produced by chromic acid, succinic acid, alkaline benzoates, or tincture of galls.—Those salts of cadmium which are insoluble in water dissolve in sulphuric, hydrochloric, or nitric acid, and likewise in cold aqueous solution of sulphate, hydrochlorate, nitrate, or benzoate of ammonia.

c. With Ammonia and with Borax.

CADMIUM AND CARBON.

CARBONATE OF CADMIC OXIDE, or CADMIC CARBONATE.—White powder, anhydrous after drying, insoluble in water. (Stromeyer.) Specific gravity about 4·4938. (Karsten.)

			Stromeyer.	John.
CdO	64	74·42	74·547	72
CO^2	22	25·58	25·453	25
HO				2
CdO,CO^2	86	100·00	100·000	99

¶ According to Lefort (*J. Pharm.* [3] 12, 406), the precipitate thrown down from cadmium solutions by alkaline carbonates is $2(CdO, CO^2) + HO$; and the whole of the water goes off between 80° and 120°.

Cadmium and Boron.

Borate of Cadmic Oxide or Cadmic Borate.—By precipitating monosulphate of cadmic oxide with borax. White powder, difficultly soluble in water. Contains 72·115 cadmic oxide and 27·885 boracic acid. (Stromeyer.)

Cadmium and Phosphorus.

A. Phosphide of Cadmium.—Grey, with a faint metallic lustre; very brittle and difficult to fuse. When heated in the air, it burns with a bright flame, and is converted into phosphate of cadmic oxide. Dissolves in hydrochloric acid, with evolution of phosphuretted hydrogen.

B. Hypophosphite of Cadmic Oxide or Cadmic Hypophosphite.—Aqueous hypophosphorous acid, saturated in the cold with excess of cadmic carbonate, then filtered and evaporated in vacuo, yields small crystals. These crystals, when heated in a retort, give off a considerable quantity of phosphorus in the form of a sublimate, and likewise a mixture of hydrogen and phosphuretted hydrogen—each bubble of which takes fire spontaneously—and leave a mixture of not quite 1 part of brown phosphoric oxide, and somewhat more than 99 parts of cadmic phosphate, in which 56·86 parts of cadmic oxide are united with 43·14 parts of phosphoric acid. (H. Rose, *Pogg.* 12, 91.)

C. Phosphite of Cadmic Oxide or Cadmic Phosphite.—By double affinity, with sulphate of cadmic oxide and phosphite of ammonia. The white precipitate, ignited in a retort, gives off pure hydrogen gas, without evolution of light and heat, but with sublimation of a small quantity of metallic cadmium, and leaves a fused mass, black and blistered when solidified. (H. Rose, *Pogg.* 9, 41.)

D. Ordinary Phosphate of Cadmic Oxide or Cadmic Phosphate.—By precipitating a cadmic salt with diphosphate of soda. White powder, insoluble in water. When heated to incipient whiteness, it fuses to a transparent glass. Contains 69·284 cadmic oxide and 30·716 phosphoric acid. (Stromeyer.)

¶ E. Pyrophosphate of Cadmic Oxide or Cadmic Pyrophosphate.—By precipitating sulphate of cadmic oxide with pyrophosphate of soda. White powder, which sinks slowly to the bottom of the liquid—soluble in ammonia, pyrophosphate of soda, and acids, but insoluble in caustic potash. When ignited in a current of hydrogen, it yields a sublimate of metallic cadmium and phosphorous acid, while a small quantity of phosphuretted hydrogen is evolved, and a white mass is left, containing phosphoric acid and cadmic oxide. It dissolves in sulphurous acid, and is precipitated from the solution, on boiling, in laminæ having a mother-of-pearl lustre.

					Schwarzenberg.
$2CdO$	128·0	....	64·19	.....	63·65
bPO^5	71·4	....	35·81	.....	36·35
$2CdO,bPO^5$	199·4	....	100·00	.....	100·00

(Schwarzenberg, *Ann. Pharm.* 65, 153.) ¶

F. METAPHOSPHATE OF CADMIC OXIDE OF CADMIC METAPHOSPHATE. —Nitrate of cadmic oxide mixed, first with metaphosphoric acid, and then with ammonia, yields a precipitate which dissolves in excess of ammonia, but separates again when the solution is exposed to the air. (Persoz, *Ann. Chim. Phys.* 56, 334.)

CADMIUM AND SULPHUR.

A. SULPHIDE OF CADMIUM.—Found native in the form of *Greenockite.* Prepared as a pigment known by the name of *Jaune brillant.* Formed with difficulty by fusing cadmium with sulphur,—more readily by igniting cadmic oxide with sulphur; precipitated in yellow flakes when hydrosulphuric acid or an alkaline hydrosulphate is brought in contact with a cadmium salt. The native sulphide crystallizes in double six-sided pyramids and other forms of the hexagonal system; cleavage parallel to the terminal and lateral edges of a six-sided prism. Specific gravity, 4·8 (Brooke), 4·908 (Breithaupt). Hardness equal to that of calcspar. Of diamond lustre, semi-transparent, honey-yellow; yields an orange-yellow or a brick-red powder; becomes carmine-red whenever it is heated. Decrepitates when heated somewhat strongly. (Brooke, Breithaupt.) The artificial sulphide, in the precipitated state, is an orange-yellow powder, which, when heated to redness, becomes first brownish and then carmine-red. Fuses at an incipient white heat, and solidifies on cooling, in transparent, lemon-yellow, micaceous laminæ. Not volatile at any temperature. (Stromeyer.) Specific gravity of the fused artificial sulphide, 4·605. (Karsten.)

			Stromeyer. *Artificial.*	Connell. *Native.*	Thomson. *Native.*
Cd	56	77·77	78·02	77·30	77·6
S	16	22·22	21·98	22·56	22·4
Fe				trace	
CdS	72	100·00	100·00	99·86	100·0

In dilute hydrochloric acid it dissolves with difficulty, even when the acid is heated; but if the acid be strong, the sulphide dissolves with ease, even at ordinary temperatures, with violent evolution of sulphuretted hydrogen, and without separation of sulphur. (Stromeyer.) At a red heat, it slightly decomposes vapour of water; at a white heat, cadmic oxide is formed. (Reynault.) Dissolves in nitric acid, with evolution of sulphuretted hydrogen and separation of sulphur. (Meissner.) Very slightly soluble in ammonia. (Wackenroder, *Repert.* 46, 226.)

B. SULPHITE OF CADMIC OXIDE OF CADMIC SULPHITE. — Cadmium dissolves in aqueous sulphurous acid, and forms sulphite of cadmic oxide, a large quantity of sulphide of cadmium being produced at the same time: for the hydrogen gas evolved by the action of the sulphurous acid on the metal, acts while in the nascent state on a portion of the sulphurous acid, and forms hydrosulphuric acid; and this, again, precipitates a portion of the dissolved cadmic oxide in the form of sulphide. (Fordos & Gélis, *Compt. rend.* 16, 1070; also *J. pr. Chem.* 29, 288.)

$$3Cd + 3HO + 3SO^2 = 3(CdO,SO^2) + 3H;$$

and

$$3H + SO^2 = HS + 2HO;$$

and

$$3(CdO,SO^2) + HS = 2CdO,3SO^2 + CdS + HO.$$

¶ Carbonate of cadmic oxide is readily dissolved by sulphurous acid; and, on adding absolute alcohol to the solution, a precipitate resembling alumina is produced, which does not give off water when heated in a tube. If this precipitate be left at rest in the liquid, beautiful silvery crystals are deposited, having the following composition:

					Muspratt.
CdO	64	....	55·99		
SO^2	48	....	28·19	.....	27·98
2HO	18	....	15·82	.....	15·90
$CdO,SO^2+2Aq.$	130	....	100·00		

(Muspratt, *Phil. Mag.* 11, 414; *Ann. Pharm.* 64, 242.) ¶

C. Hyposulphate of Cadmic Oxide or Cadmic Hyposulphate.—The solution of cadmic carbonate in aqueous hyposulphuric acid deposits, when slowly cooled, a crystalline mass of salt, which has a very rough taste, is very easily soluble in water, and deliquesces in moist air.

D. Sulphate of Cadmic Oxide or Cadmic Sulphate.—*a. Disulphate.*—1. By ignition of *b.* (Stromeyer.)—2. By imperfectly precipitating *b* with potash (Kühn, *Schw.* 60, 344);—by exactly precipitating one-third of a solution of the neutral sulphate with caustic potash, and boiling the precipitate with the rest of the solution. (Kühn, *Pharm. Centr.* 1847, 595.) Sparingly soluble in water; separates from the solution in scales. (Stromeyer.)

					Kühn (1.)		Kühn (2.)
2CdO	128	....	72·32	.....	72·01	....	72·6
SO^3	40	....	22·60	.....	21·96	....	19·3
HO	9	....	5·08	.....	6·03	....	8·1
$2CdO,SO^3+Aq.$	177	....	100·00	.....	100·00	....	100·0

b. Monosulphate.—Crystallizes with water in large, transparent rectangular prisms, resembling crystals of zinc-vitriol; they effloresce rapidly in the air [permanent in the air, according to Meissner], and, when gently heated, give off their water of crystallization without fusing; when more strongly ignited, they lose half their acid, and are converted into *a.* Easily soluble in water. (Stromeyer.)

	Anhydrous.				Stromeyer.		*Crystallized.*				Stromeyer.
CdO.....	64	....	61·54	....	61·7	CdO....	64	....	45·72	....	45·956
SO^3.....	40	....	38·46	....	38·3	SO^3	40	....	28·57	....	28·523
						4HO....	36	....	25·71	....	25·521
CdO,SO^3	104	....	100·00	....	100·0	+4Aq.	140	....	100·00	....	100·000

¶ By evaporating a solution of cadmic sulphate containing excess of sulphuric acid, Kühn obtained compact crusts of indistinct crystals, containing CdO,SO^3+HO. (*Pharm. Centr.* 1847, 595.) ¶

E. Sulphocarbonate of Cadmium.—Hydrosulphocarbonate of calcium gives, with cadmic salts, a lemon-yellow precipitate, slightly soluble in water, to which it imparts a yellow colour. (Berzelius.)

Cadmium and Selenium.

¶ Selenite of Cadmic Oxide or Cadmic Selenite.—Selenious acid does not precipitate salts of cadmium. Selenite of ammonia gives, with chloride of cadmium, a white precipitate, having an argillaceous appearance, and assuming an orange tint when exposed to the air. The salt contains no water. It is soluble in selenious acid. When heated in a tube, it yields a yellowish-red sublimate. (Muspratt, *Chem. Soc. Qu. J.* II. 65.) ¶

Cadmium and Iodine.

A. Iodide of Cadmium.—Prepared either in the dry way or by digesting cadmium with iodine and water. Fuses very easily. Crystallizes on cooling from the fused state, or from an aqueous or alcoholic solution, in large, transparent and colourless, six-sided tables, which are permanent in the air, and have a metallic lustre inclining to that of mother-of-pearl.—When somewhat strongly ignited [in the air?], it evolves iodine. Dissolves readily in water and alcohol, and crystallizes from these solutions, on evaporation, still in the form of iodide of cadmium. Sulphuretted hydrogen passed through the solution slowly precipitates sulphide of cadmium. (Stromeyer.)

					Stromeyer.
Cd	56	....	30·77	.....	30·54
I	126	....	69·23	.....	69·46
CdI	182	....	100·00	.....	100·00

B. Iodate of Cadmic Oxide or Cadmic Iodate.—Concentrated solutions of iodate of soda and iodate of cadmic oxide immediately form a precipitate soluble in excess of the cadmic salt; it is bulky at first, but soon falls together in the form of a crystalline meal. When dry, it forms a white anhydrous powder. This powder, when heated in a retort, gives off oxygen gas and iodine vapour, and leaves a brownish-red mixture of oxide and iodide of cadmium, from which water extracts nothing, but nitric acid liberates iodine.—The powder dissolves but very sparingly in water, more readily in nitric acid and ammonia.

Cadmium and Bromine.

A. Bromide of Cadmium.—1. At ordinary temperatures, cadmium does not combine with bromine; but when heated nearly to redness, it absorbs vapour of bromine, forming white fumes of bromide of cadmium. 2. Hydrated bromide of cadmium is converted by heat into the anhydrous bromide.—Bromide of cadmium fuses readily [and crystallizes on cooling; *Croft*], and, when strongly heated, sublimes in white rounded laminæ having a mother-of-pearl lustre. It is decomposed by heated nitric acid, but dissolves without decomposition in hydrochloric acid, acetic acid, alcohol, and ether.

					Berthémot.
Cd	56·0	....	41·66	.....	41·47
Br	78·4	....	58·34	.....	58·53
CdBr	134·4	....	100·00	.....	100·00

Hydrated Bromide of Cadmium or *Hydrobromate of Cadmic Oxide.*—Bromide of cadmium dissolves easily in water. The solution may be formed by digesting cadmium with bromine and water. When evaporated and cooled, it yields white, efflorescent needles. These crystals give off half their water at 100°, and the rest, without fusing, at 200°, whereupon they assume an enamel-like appearance. (Rammelsberg, *Pogg.* 55, 241.) When suddenly heated, they fuse in their water of crystallization, and are converted into anhydrous bromide of cadmium. (Berthémot; *comp.*, Croft, *Phil. Mag. J.* 21, 356.)

	Crystallized.			Croft.	Rammelsberg.
CdBr	134·4	78·87		79·05	80·5
4HO	36·0	21·13		20·95	19·5
CdBr + 4Aq.	170·4	100·00		100·00	100·0

B. Bromate of Cadmic Oxide or Cadmic Bromate.—Formed by precipitating sulphate of cadmic-oxide with bromate of baryta, and evaporating the filtrate over oil of vitriol in a receiver containing air.—Transparent, rhombic prisms with angles of 127° and 53°, having their lateral edges truncated, and bevelled with two narrow faces; terminated with four-sided summits. The crystals, when heated, give off bromine vapour and oxygen gas, and leave a brown mixture of oxide and bromide of cadmium, the latter of which may be dissolved out by water. They dissolve in 0·8 pt. of cold water. (Rammelsberg, *Pogg.* 55, 74.)

	Crystallized.			Rammelsberg.
CdO	64·0	33·44		33·38
BrO^5	118·4	61·86		61·92
HO	9·0	4·70		4·70
$CdO, BrO^5 + Aq.$	191·4	100·00		100·00

Cadmium and Chlorine.

A. Chloride of Cadmium.—Formed by fusing the hydrochlorate of cadmic oxide. After fusion it presents the appearance of a transparent mass, having a metallic, pearly lustre and lamellated texture; crystallizes by sublimation in transparent, micaceous laminæ having a similar lustre. Fuses at a heat below redness, and volatilizes at a somewhat higher temperature.—When exposed to the air, it loses its transparency and lustre, and crumbles to a white powder. (Stromeyer.)

				Stromeyer.
Cd	56·0	61·27		61·39
Cl	35·4	38·73		38·61
CdCl	91·4	100·00		100·00

Hydrated Chloride of Cadmium or *Hydrochlorate of Cadmic Oxide.*—Transparent rectangular prisms which deliquesce readily when heated, and are easily soluble in water. (Stromeyer, John.)

Perchlorate of Cadmic Oxide or Cadmic Perchlorate.—The solution of the oxide in aqueous perchloric acid leaves, when evaporated in the hot air chamber, a transparent, deliquescent, crystalline mass, which is soluble in alcohol. (Serullas, *Ann. Chim. Phys.* 46, 305.)

Cadmium and Fluorine.

Fluoride of Cadmium.—Deposited from the aqueous solution, on evaporation, in white, indistinctly crystalline crusts, which adhere firmly to the sides of the vessel. Sparingly soluble in pure water, more readily in aqueous hydrofluoric acid. (Berzelius, *Pogg.* 1, 26.)

Cadmium and Nitrogen.

A. *Nitride of Cadmium?*—Obtained in the same manner as nitride of zinc (p. 33). The solution must always contain an excess of sal-ammoniac. The liquid becomes turbid [in the preparation of zinc-nitride it remains clear], because the ammonia, as it is set free at the negative pole, precipitates hydrated cadmic oxide, which, however, in the immediate neighbourhood of the pole, is re-dissolved by the ammonia subsequently liberated. On the negative pole there is soon deposited a spongy, dark, lead-grey, non-crystalline mass, which visibly increases, and, after being pressed between two plates of glass, has the appearance of a lead-grey amalgam: when washed and dried, it has a specific gravity of 4·8. Five grains of this substance yield, when heated, from 0·18 to 0·25 cub. in. of nitrogen gas free from hydrogen, and leave a yellowish-green residue containing globules of metallic cadmium. (Grove, *Phil. Mag. J.* 19, 99; also *Pogg.* 54, 101.)

B. Nitrate of Cadmic Oxide, or Cadmic Nitrate.—Crystallizes in combination with water, in prisms and needles united in radiated masses (Stromeyer), which deliquesce in the air (Meissner), and dissolve in alcohol, but do not impart any peculiar colour to its flame. (Children.)

	Anhydrous.		Stromeyer.		*Crystallized.*		Stromeyer.
CdO	64	54·24	54·09	CdO	64	41·56	42·15
NO^5	54	45·76	45·91	NO^5	54	35·07	35·78
				4HO	36	23·37	22·07
CdO,NO^5	118	100·00	100·00	+4Aq.	154	100·00	100·00

C. Ammoniacal Oxide of Cadmium.—Aqueous ammonia readily dissolves cadmic oxide—the oxide first turning white—and deposits it, on evaporation, in the form of a gelatinous hydrate. (Stromeyer.)—Potash precipitates cadmic oxide from its solution in ammonia.

D. Ammoniacal Hyposulphate of Cadmic Oxide.—The solution of cadmic hyposulphate in heated ammonia, when left to evaporate spontaneously, deposits the compound in the form of a crystalline meal, mixed, however,—since some amount of decomposition takes place on evaporation—with hydrate and hyposulphate of cadmic oxide. (Rammelsberg, *Pogg.* 58, 298.)

			Rammelsberg.
$2NH^3$	34	20·00	18·32
CdO	64	37·65	38·12
S^2O^5	72	42·35	
$2NH^3+CdO,S^2O^5$	170	100·00	

E. Ammonio-sulphate of Cadmic Oxide.—100 parts of anhydrous cadmic sulphate absorb 48·69 parts (3 At.) of ammonia, with great rise of temperature and tumefaction, and are thereby converted into a white powder. The compound, when heated to redness, gives off a large quantity of ammoniacal gas, and yields a trifling sublimate of sulphite of ammonia. It dissolves in water, with separation of cadmic oxide. (H. Rose, *Pogg*, 20, 152.)

					H. Rose.
$3NH^3$	51	....	32·9	.....	32·74
CdO,SO^3	104	....	67·1	.....	67·26
$3NH^3 + CdO,SO^3$	155	....	100·0	.....	100·00

F. Ammonio-iodide of Cadmium.—*a.* $3NH^3,CdI$.—Dry iodide of potassium does not absorb ammoniacal gas at ordinary temperatures; but when gently heated, it takes up 27·789 per cent. of ammonia, swelling up and evolving heat, and crumbling to a fine white powder. The compound gives up all its ammonia when heated. Water added to the powder separates hydrated oxide of cadmium, with which a small portion of iodine still remains—and forms a solution containing a small portion of cadmium, and giving off ammonia when heated. (Rammelsberg.)

b. NH^3,CdI.—A solution of iodide of potassium in heated ammonia deposits very small crystals on cooling, and the mother-liquid, if evaporated and mixed with ammonia, yields an additional quantity. The crystals fuse when heated, giving off ammonia and water—which is not essential to their constitution—and leaving iodide of cadmium. They are decomposed by water in the same manner as *a*. (Rammelsberg, *Pogg*. 48, 153.)

		a.			Rammelsberg.
$3NH^3$	51	....	21·89	.....	21·75
CdI	182	....	78·11	.....	78·25
$3NH^3,CdI$	233	....	100·00	.....	100·00

		b.			Rammelsberg.
NH^3	17	....	8 54	.....	7·15
CdI	182	....	91·46	.....	91·37
HO		....		.....	1·48
NH^3,CdI	199	....	100·00	.....	100·00

When a solution of cadmic iodate in aqueous ammonia is left to evaporate freely, it yields—besides crystals of iodate of ammonia—crystalline crusts, which probably contain ammoniacal iodate of cadmic oxide. (Rammelsberg.)

G. Ammonio-bromide of Cadmium.—*a.* $2NH^3,CdBr$. Dry, pulverized bromide of cadmium swells up when introduced into ammoniacal gas, taking up 2 atoms of ammonia (from 2 to 3: *Croft.*), and crumbling to a bulky white powder. The compound gives off all its ammonia when heated; on dissolving it in water, part of the oxide separates out. (Rammelsberg.)—*b.* $NH^3,CdBr$. A concentrated solution of bromide of cadmium saturated with ammonia, yields, on evaporation, small crystals, which behave like *a* when heated, or when digested in water. (Rammelsberg, *Pogg*. 55, 241.) A solution of bromide of cadmium in warm aqueous ammonia deposits the compound in crystalline grains when rapidly cooled, and in regular octohedrons by slow cooling. (Croft, *Phil. Mag. J.* 21, 356.)

		a.		Rammelsberg.
$2NH^3$	34·0	20·19		22·26
Cd	56·0	33·25		77·74
Br	78·4	46·56		
$2NH^3,CdBr$	168·4	100·00		100·00

		b.		Rammelsberg.	Croft.
NH^3	17·0	11·23		10·66	11·69
Cd	56·0	36·99		38·19	
Br	78·4	51·78			
$NH^3,CdBr$	151·4	100·00			

H. Ammonio-bromate of Cadmic Oxide.—The concentrated solution of cadmic bromate, mixed with a quantity of ammonia sufficient to re-dissolve the precipitate formed by the first portions, and then evaporated under a receiver containing lime, yields crystals. The mixture is decomposed, both when evaporated by heat, and when diluted with water,—white flakes of hydrated cadmic oxide, free from bromine, being deposited. (Rammelsberg, *Pogg.* 55, 74.)

	Calculation.	
$3NH^3$	51·0	12·27
2CdO	128·0	30·78
$2BrO^5$	236·8	56·95
$3NH^3+2(CdO,BrO^5)$	415·8	100·00

I. Ammonio-chloride of Cadmium.—*a.* $3NH^3,CdCl$.—100 parts of pulverized dry chloride of cadmium absorb 53·56 parts (about 3 At.) of ammonia, the absorption being slow at first, but afterwards rapid, and attended with rise of temperature and tumefaction. The compound, when exposed to the air, gives off ammonia till it has lost its odour, and is converted into the following compound :—*b.* $NH^3,CdCl$.—Chloride of cadmium treated with aqueous ammonia yields a white powder, which dissolves on the application of heat, and is deposited in the form of a crystalline powder on cooling. When heated, it gives off 16·63 per cent. (1 At.) of ammonia, mixed, however, with a small portion of sal-ammoniac; consequently, the residue is no longer soluble in water. (Croft, *Phil. Mag. J.* 21, 355.)

K. Chloride of Cadmium and Ammonium.—$NH^4Cl,CdCl$.—A concentrated solution of chloride of cadmium and sal-ammoniac in equal numbers of atoms yields, at first, silvery needles containing 1 atom of water; these, however, gradually disappear, and are replaced by large anhydrous rhombohedrons, slightly soluble in alcohol and wood-spirit. (Croft.)

Pure hydrated *Carbonate* and *Phosphate of Cadmic Oxide* dissolve readily in sulphate, hydrochlorate, nitrate, and succinate of ammonia. (Wittstein, *Repert.* 57, 32.)

Cadmium and Potassium.

A. Sulphate of Cadmic Oxide and Potash.—Yields crystals having the form of sulphate of magnesia and ammonia. (Mitscherlich.)

B. Iodide of Cadmium and Potassium.—KI,CdI.—Not crystallizable; very easily soluble in water,—slightly soluble in alcohol and wood-spirit. (Croft.)

C. Bromide of Cadmium and Potassium.—KBr,CdBr.—Hydrated needles, very easily soluble in water, slightly soluble in alcohol. (Croft.)

D. Chloride of Cadmium and Potassium.—KCl,CdCl.—Yields anhydrous and hydrated crystals, analogous to those of chloride of cadmium and ammonium. Dissolves in water less readily than C; slightly soluble in alcohol and wood-spirit. (Croft.)

Cadmium and Sodium.

Carbonate of soda does not dissolve cadmic oxide before the blowpipe.

A. Melted *Borax* dissolves the oxide, forming a clear glass, which is yellowish while hot, becomes almost colourless on cooling, and if moderately charged with oxide, becomes milk-white by gentle flaming, but if more strongly charged, assumes an enamel-white appearance on simple cooling; if heated on charcoal, it boils continuously in consequence of the reduction and volatilization of the cadmium.

B. *Microcosmic Salt* dissolves the oxide abundantly, forming a clear glass, which, if saturated, becomes milk-white on cooling. (Berzelius.)

C. Chloride of Cadmium and Sodium.—NaCl, CdCl.—Warty crystals, containing 3 At. water, soluble in 1·4 parts of water at 16°; slightly soluble in alcohol and wood-spirit. (Croft.)

Cadmium and Calcium.

Hypophosphite of Cadmic oxide and Lime?—By boiling cadmic oxalate in excess with hypophosphite of lime and water, and evaporating the filtrate in vacuo, a crystalline mass is obtained, which, when heated in a retort, gives off spontaneously inflammable phosphuretted hydrogen gas, a character by which it is distinguished from pure cadmic hypophosphite. It contains: hypophosphite of lime, 3·74; hypophosphite of cadmic oxide, 68·80; water, 27·46 (4 At.). (H. Rose, *Pogg.* 12, 294.)

Cadmium and Silicium.

Hydrated Silico-Fluoride of Cadmium.—Long, transparent, and colourless prisms, which are very easily soluble in water, and effloresce in warm air, forming an opaque, easily disintegrated mass. (Berzelius, *Pogg.* 1, 199.)

Cadmium and Tungsten.

A. Tungstate of Cadmic Oxide.—*a. Monotungstate.*—Monotungstate of potash or soda added to a cadmic salt, throws down a white powder, which gives off its water when heated, assuming a reddish or yellowish

colour, and afterwards, when heated to redness, becomes bluish-black, and bakes together into a hard mass. It dissolves in phosphoric acid, oxalic acid, and ammonia, but not in water.—*b. Bitungstate.* By precipitating with an alkaline bitungstate. The white pulverulent precipitate is anhydrous; when ignited, it turns grey and bakes together. Soluble in phosphoric, oxalic, acetic acid, and ammonia, but not in water. (Anthon, *J. pr. Chem.* 9, 341.)

	a.	*Ignited.*	Anthon.
CdO	64	34·78	35·87
WO^3	120	65·22	64·13
CdO,WO^3	184	100·00	100·00

	a.	*Hydrated.*	Anthon.
CdO	64	31·68	33
WO^3	120	59·41	59
2HO	18	8·91	8
$CdO,WO^3+2Aq.$	202	100·00	100

B. Sulphotungstate of Cadmium.—CdS,WS^3.—On mixing the solution of a cadmic salt with sulphotungstate of potassium, this compound is immediately precipitated in the form of a lemon-yellow powder. (Berzelius.)

Cadmium and Molybdenum.

A. Molybdate of Cadmic Oxide.—Molybdate of ammonia gives, with sulphate of cadmic oxide, a greyish white precipitate which turns brown when gently ignited. (Brandes.)

B. Sulphomolybdate of Cadmium.—By precipitating a cadmic salt with sulphomolybdate of potassium. Dark-brown precipitate, insoluble in water. (Berzelius.)

C. Persulphomolybdate of Cadmium.—By precipitating with persulphomolybdate of potassium. Red precipitate. (Berzelius, *Pogg.* 7, 286.)

Cadmium and Vanadium.

Vanadiate of Cadmic Oxide.—*a. Monovanadiate.*—On mixing concentrated solutions of an alkaline monovanadiate and a cadmic salt, a portion is immediately precipitated in the form of a yellow substance which gradually turns white; the greater part of the salt is subsequently deposited as a white crystalline crust.—*b. Bivanadiate.*—Soluble in water. (Berzelius.)

Permanganate of Potash does not precipitate hydrochlorate of cadmic oxide.

Cadmium and Arsenic.

A. Sulpharsenite of Cadmium.—By precipitating a cadmic salt with a saturated solution of sulpharsenious acid in hydrosulphate of ammonia. The pale yellow precipitate—orange-yellow when dry—becomes semi-fluid when heated, and is converted, by loss of orpiment,

into a swollen, metal-grey compound of sulphide of cadmium with a small quantity of orpiment, which forms a deep-yellow powder. (Berzelius, *Pogg.* 7, 146.)

B. SULPHARSENIATE OF CADMIUM.—Aqueous sulpharseniate of sodium gives a light yellow precipitate with cadmic salts. (Berzelius, *Pogg.* 7, 88.)

CADMIUM AND ANTIMONY.

SULPHANTIMONIATE OF CADMIUM.—The solution of Schlippe's salt gives a light orange-yellow precipitate with cadmic salts, if the former be in excess; but if the cadmic salt is in excess, the precipitate is darker in colour and becomes red-brown after remaining for some time immersed in the liquid. (Rammelsberg, *Pogg.* 52, 236.)

CADMIUM AND TELLURIUM.

SULPHOTELLURITE OF CADMIUM.—Analogous to the cerium-compound (IV. 425).

OTHER COMPOUNDS OF CADMIUM.

With Copper, Mercury, and Platinum.

CHAPTER XXX.

TIN.

Proust. *J. Phys.* 51, 173; also *Scher. J.* 8, 481.—*J. Phys.* 61, 338; also *N. Gchl.* 1, 249; also *Gilb.* 25, 440.
Berzelius. *Schw.* 6, 284.—Further: *Ann. Chim. Phys.* 5, 141; also *N. Tr.* 2, 2, 359.
J. Davy. *Schw.* 10, 321.
Gay-Lussac. *Ann. Chim. Phys.* 1, 40.

SYNONYMES: *Etain, Zinn, Stannum, Jupiter.*

History. Tin was known in the metallic state as early as the time of Moses; it was imported by the Phœnicians from Spain and England. Bichloride of tin was discovered in the sixteenth century by Libavius. The preparation of Mosaic gold was taught by Kunkel. The chief contributions to our knowledge of the compounds of tin have been made by Pelletier, Proust, J. Davy, and Berzelius.

Sources. Most frequently, as binoxide, in Tin-stone; rarely with sulphur and copper, in Tin-pyrites. In very small quantities, as binoxide, in the Seidschütz water, and in many meteoric stones (Berzelius); in Manganesian Epidote and native peroxide of manganese (*Braunstein*) from Piedmont, and in all Scandinavian Epidotes. (Sobrero.)

Preparation on the large scale. Tin-stone is broken up—roasted to drive off the sulphur and arsenic of the ores that are mixed with it, and convert the other metals into light oxides easily separated from the heavier tin-stone by washing—and then fused in contact with charcoal, either in smelting furnaces or in reverberatory furnaces, sometimes with the addition of a calcareous flux.—*Purification on the large scale.*—1. By gentle heating, whereby the purer tin fuses and runs off, while the more refractory alloys of tin and the foreign metals remain unmelted.—2. By fusion, with imperfect access of air, whereby the foreign metals, together with a portion of the tin, are oxidized first.—The purest varieties of tin are *Malacca* and *Banca tin* and *English Grain-tin;* then follows *Common English Grain-tin;* then English *Block-tin* and *Saxon* and *Bohemian Mine-tin* (*Bergzinn*); then *Tin-refuse* and *Tin-scum* (*Abgangs-und Abstrich-zinn*). The impurities consist of arsenic, antimony, bismuth, zinc, lead, iron and copper; they remain for the most part in the form of a black powder, on dissolving the tin in hydrochloric acid. The greater part of the arsenic is, however, evolved in the form of arseniuretted hydrogen gas, and may be detected by Marsh's process. Stüremberg (*Ann. Pharm.* 29, 216) found arsenic in all commercial tin, and likewise in tin-foil and tin-plate; a sample of Banca tin and likewise of English grain-tin were, however, found to be free from arsenic. Chevallier (*J. Chim. Méd.* 16, 250) likewise obtained arseniuretted hydrogen gas on dissolving Banca tin which was said to be free from arsenic and did not deposit any black powder when dissolved.—*Purification on the small scale.*—This is effected by oxidizing tin-filings with excess of nitric acid, washing the resulting binoxide with hydrochloric acid and water, and reducing it in a closed charcoal crucible at a low white heat. If pure water be used in the washing, the stannic oxide retains oxide of copper.

Properties. Crystalline system the square prismatic. When a feeble current from a Daniell's battery (I. 421) is passed through aqueous hydrochlorate of stannous oxide, the positive pole being formed of a plate of tin, the negative polar wire becomes covered, in the course of four days, with perfect crystals belonging to the square prismatic system. *Fig.* 39, without the *p* face, but having the four *a*-faces and likewise eight acumination-faces resting upon *e* and *a*. Macle-crystals are of frequent occurrence. (Miller, *Phil. Mag. J.* 22, 263.) Mather (*Sill. Ann. J.* 27, 254) likewise obtained right-angled four-sided crystals of metallic tin, upon a piece of the metal immersed in a solution of the protochloride. Brooke obtained eight-sided needles by slowly cooling melted tin, and pouring off the portion which remained liquid. Pajot, on the other hand (*J. Phys.* 38, 52), obtained rhombic tables by this process; and Breithaupt (*Schw.* 52, 171) saw tin from a Cornwall tin-furnace crystallized in short, regular, six-sided prisms. These crystals were regarded by Miller as $CuSn^2$. Frankenheim (*Pogg.* 40, 456) concludes, from the angles of the dendrites in the tin-tree, that the crystals belong to the regular system.—Specific gravity of tin-crystals $=7{\cdot}178$, and after fusion and solidification, 7·293 (Miller); of tin solidified from fusion, 7·291 (Brisson), 7·2911 (Kupffer), 7·2905 (Karsten); of rolled tin, 7·299 (Brisson). Softer than gold, harder than lead; fracture indented. Decrepitates when bent. This crackling of tin (*Geshrei des Zinns*) is produced by the displacement of the crystals of which it is made up. Tin cannot be drawn out into fine wire, but may be beaten out into thin plates (*Tin-foil*). Bluish-white, with a strong lustre. Melts at 222·5°

(G. A. Erman), at 238° (Crichton), at 230° (Kupffer), at 267° (Morveau), and contracts slightly in cooling (Marx). Boils at a white heat. The disagreeable odour ascribed to tin does not properly belong to the metal itself, but is solely due to its action on animal substances, the fingers for example, with which it comes in contact.—Nitric acid of moderate strength attacks tin with violence, but without dissolving it, and converts it into a white powder. Tin may also be easily distinguished from other metals by its behaviour with a solution of gold containing excess of hydrochloric acid; a bright surface of tin immersed in such a solution, is blackened without evolution of gas; zinc turns black and liberates gas; lead does not blacken. (Friedemann, *Repert.* 77, 224.)

Compounds of Tin.

Tin and Oxygen.

A. Stannous Oxide. SnO.

Protoxide of Tin, Zinnoxydul, Oxyde Stanneux.

Formation. Tin slowly decomposes water mixed with hydrochloric acid, sulphuric acid, or potash, and dissolves in these substances in the form of stannous oxide. The hydrogen which is evolved contains arsenic, if that metal is present in the tin. The aqueous solutions of sal-ammoniac, common salt, bisulphate of potash, alum, cream of tartar and borax-tartar likewise dissolve small quantities of tin when heated, and form solutions of stannous oxide; tin is also dissolved, though in very small quantity, by the aqueous solutions of nitrate of soda, monotartrate of potash, and Rochelle salt. Solutions of carbonate of potash, sulphate of soda, chloride of barium or calcium, sulphate of magnesia, and tartrate of potash and ammonia do not retain tin in solution, but in contact with air produce a deposition of stannic oxide. Nitre, borax, and diphosphate of soda have no action upon tin. (Lindes, *Berl. Jahrb.* 32, 2, 99; Cludius, *J. pr. Chem.* 9, 161.)

Preparation. 1. Stannous oxide is precipitated in the form of hydrate from its solution in hydrochloric acid by the addition of carbonate of potash in excess—the hydrate quickly washed with thoroughly boiled water, and as much as possible out of contact of air—then dried at a temperature not exceeding 80°—and lastly freed from water by heating it in a retort completely filled with it, and having the air replaced by hydrogen or carbonic acid gas. (Berzelius.)—2. Hydrochlorate of stannous oxide is treated with excess of ammonia, and the precipitated hydrate of stannous oxide boiled quickly for awhile to convert it into the anhydrous oxide, which is then quickly washed and dried. (Gay-Lussac.)—3. Aqueous hydrochloric acid is saturated with tin; the solution evaporated in contact with a piece of metallic tin, till a residue of fused protochloride of tin is left; the metal then taken out; 1 At. of the chloride of tin (94·4 parts) mixed in a mortar with 1 At. (143·2 parts) or more of crystallized carbonate of soda; the fluid mixture heated in a basin—with constant stirring—till it has become black through and through; the chloride of sodium, after cooling, extracted with boiling water; the stannous oxide washed with boiling water on the filter, and

lastly dried at a gentle heat. (Sandall, *Phil. Mag. J.* 12, 216; also *J. pr. Chem.* 14, 254.) This is a very advantageous mode of preparation. (Böttger, *Ann. Pharm.* 29, 87.)

Properties. Black powder, of specific gravity 6·666; brown-greenish-grey when pounded. (Berzelius.) Olive-green. (Gay-Lussac.) Bluish-black or slate-grey. (Sandall.) When hydrate of stannous oxide is boiled with a quantity of potash not sufficient to dissolve it, the undissolved portion is converted into small, hard, shining, black crystals of anhydrous stannic oxide, which, when heated to 200°, decrepitate, swell up, and fall to pieces, and are converted into the olive-green protoxide like that obtained by Gay-Lussac. On evaporating a very dilute solution of sal-ammoniac in which hydrated protoxide of tin is diffused, that compound is converted, as soon as the sal-ammoniac crystallizes, into the anhydrous protoxide, having the form of a cinnabar-coloured powder, which, by friction with a hard body, is immediately converted into the greenish-brown binoxide. There are therefore three modifications of stannous oxide: crystallized, olive-green, and red. (Fremy, *Compt. rend.* 15, 1107; also *N. J. Pharm.* 3, 28.)—¶ Roth (*Ann. Pharm.* 60, 214) obtains the red modification by thoroughly washing the white hydrate of stannous oxide and digesting it at a temperature of 56° with a solution of that oxide in acetic acid, the acid being slightly in excess and the solution having a specific gravity of 1·06. The stannous oxide is then converted into heavy, hard, crystalline grains which yield a greenish-brown powder by trituration; they take fire when heated, and soon blacken by exposure to sunshine. With chemical re-agents, they behave like stannous oxide. ¶

			Berzelius.	J. Davy.	Gay-Lussac.	Proust.
Sn	59	88·06	88·028	88·01	88·106	87
O	8	11·94	11·972	11·99	11·894	13
SnO	67	100·00	100·000	100·00	100·000	100

(SnO = 735·29 + 100 = 835·29. Berzelius.)

Decompositions. Reduced to the metallic state, by charcoal at a strong red heat; by potassium at a moderate heat, and with combustion. By sulphur it is converted into sulphide of tin, with evolution of sulphurous acid; and by boiling with a small quantity of potash-ley, into metallic tin and stannic acid, the latter dissolving in the potash.

Combinations. *a.* With Water.—Hydrate of Stannous Oxide. When a solution of protochloride of tin is mixed with excess of carbonate of potash, or with excess of ammonia, the hydrated protoxide is precipitated in the form of a brilliant white powder, containing, according to Proust, 5 per cent. of water, which, according to Berzelius, it gives up when gently heated, or even when boiled with water.—¶ According to Schaffner, the precipitate formed by ammonia is not the hydrate, but a basic salt. The composition of the hydrate is 2SnO,HO. ¶

b. With Acids, forming the Salts of Stannous Oxide or Stannous Salts.—*Protosalts of Tin.*—These salts are obtained by dissolving metallic tin, the protoxide, or its hydrate—which is more easily soluble—in acids. Most of them are either colourless or yellowish, redden litmus, and have a very disagreeable metallic taste. They rapidly abstract oxygen from the air and other oxygen compounds, and are thereby converted into stannic salts; hence they give a purple or brown

precipitate with chloride of gold, &c. [For a more detailed description of this, vid. *Protochloride of Tin.*] Those which contain a volatile acid, give it off at a red heat, and, if the air has access to them, are converted into stannic oxide. With carbonate of soda upon charcoal in the inner blowpipe-flame, they yield globules of metallic tin.—Zinc and cadmium immersed in the aqueous solutions of these salts precipitate the tin in an arborescent form: *the Tin-tree, Arbor Jovis.* Acetate of stannous oxide, however, is not reduced by tin or cadmium. Iron reduces the tin from the hydrochlorate and acetate, provided the iron is made to dip into water in which is likewise immersed a bladder containing the tin-solution, so that the latter may mix very slowly with the water by endosmose. Iron does not precipitate tin from the protochloride at a boiling heat. Lead, when first immersed, reduces a small quantity of tin in brilliant needles, but the action soon ceases. (Fischer, *Pogg.* 9, 263; 10, 603.) Hydrosulphuric acid gas and hydrosulphate of ammonia precipitate dark-brown hydrated protosulphide of tin. This precipitate dissolves in a large excess of hydrosulphate of ammonia—provided that compound likewise contains hydrosulphite of ammonia—and is precipitated from the solution by acids in the form of yellow bisulphide of tin. (H. Rose.) —Hydrosulphuric acid gives no precipitate in a solution containing less than 1 part of tin in 120,000 parts of water. (Pfaff.)—A solution of 1 part of crystallized hydrochlorate of stannous oxide in 100 parts of water, mixed with 15 parts of hydrochloric acid of specific gravity 1·168, is immediately precipitated by hydrosulphuric acid; with 25 parts of hydrochloric acid, not till after some time; with 40 parts of hydrochloric acid, not at all, but immediately on adding more water. (Reinsch. *J. pr. Chem.* 13, 132.)—Iodide of potassium gives a yellowish-white curdy precipitate, which, if the tin and iodine are in proper proportion and the solution duly concentrated, is soon converted into protiodide of tin. Ammonia, carbonate of ammonia, and carbonate of potash throw down the white hydrate of stannous oxide, insoluble in excess of these precipitants.—An excess of potash, on the contrary, re-dissolves the precipitated hydrate, forming a solution, which deposits metallic tin in the form of a black powder, slowly in the cold, rapidly when heated, stannate of potash being formed and remaining in solution.—Phosphate of soda throws down white phosphate of stannous oxide.—Oxalic acid throws down white oxalate of stannous oxide.—Croconate of potash gives an orange-yellow precipitate with stannous salts.—Succinic acid and the alkaline benzoates, according to Pfaff, give white precipitates to the ten-thousandth degree of dilution.—Tincture of galls produces, in solutions not containing a very great excess of acid, an abundance of light-yellow flakes.—Ferrocyanide and ferricyanide of potassium produce white precipitates soluble in hydrochloric acid.—Stannous salts which are insoluble in water, dissolve in hydrochloric acid—provided they have not been ignited—but not in sal-ammoniac.

c. With Potash and Soda.

Oxides of Tin, intermediate between Stannous and Stannic Oxide.

a. Sesquioxide. Sn^2O^3.—1. Aqueous hydrochlorate of stannous oxide, somewhat in excess, is boiled with freshly precipitated hydrate of ferric oxide or hydrate of manganic oxide, and the precipitated sesquioxide of tin thoroughly washed. (Fuchs, *Kastn. Arch.* 23, 368.)—

$$Fe^2O^3 + 2SnCl = Sn^2O^3 + 2FeCl.$$

The precipitate is frequently mixed with hydrated ferric oxide. (Berzelius.) The hydrated ferric oxide, even when recently precipitated, acts much less quickly in the cold than at a boiling heat; the dried hydrate requires continued boiling; finely pounded specular iron acts but very imperfectly at a boiling heat. Even when the hydrochlorate of stannous oxide contains no free acid, a small quantity of iron is dissolved at the beginning of the action, before the precipitation of the sesquioxide of tin takes place. If the hydrated ferric oxide be briskly boiled with excess of stannous hydrochlorate, the precipitate which forms at first is re-dissolved after a while, but appears again on the addition of water; under these circumstances, however, the sesquioxide of tin is contaminated with bibasic hydrochlorate of stannous oxide.—Pulverized Pyrolusite acts but very slowly, even on boiling; but if the liquid be boiled down nearly to dryness,—whereupon a large quantity of hydrochloric acid is evolved, but no chlorine—and the residue dissolved in water, sesquioxide of tin separates from the solution, mixed with pyrolusite. (Fuchs.)—2. Hydrochlorate of stannous oxide is mixed with hydrochlorate of ferric oxide, and as soon as the yellow-colour of the mixture has changed to greenish, the hydrated oxide is precipitated from it by adding carbonate of lime in excess, and applying a gentle heat. (Fuchs, *J. pr. Chem.* 5, 318.)—3. A solution of hydrochlorate of stannous oxide, saturated as far as possible with ammonia, is mixed in excess with the dark red solution of basic hydrochlorate of ferric oxide,—obtained by saturating aqueous hydrochlorate of ferric oxide with recently precipitated hydrate of ferric oxide, or by mixing the aqueous solution of the hydrochlorate of ferric oxide with as much ammonia as can be added to it without producing a permanent precipitate—and the mixture heated to 60° in a vessel completely filled with it. The liquid, which is dark brown at first, gradually loses its colour, and the hydrated sesquioxide of tin is precipitated free from iron. (Berzelius, *Pogg.* 28, 443.)—White, with a tinge of yellow. (Fuchs.) The precipitate, which is gummy and difficult to wash, dries up to a mass of yellow, translucent granules. The hydrate turns black when ignited out of contact of air. It dissolves completely in ammonia, and is therefore not a mere mixture of stannic and stannous oxides, inasmuch as the latter is insoluble in ammonia. (Berzelius.)—[Probably, however, it is a salt—SnO,SnO^2, containing the soluble modification of stannic acid.]

b. Anomalous Stannate of Stannous Oxide.—When hydrated stannic oxide, obtained by treating tin with nitric acid, is digested in cold aqueous hydrochlorate of stannous oxide, it abstracts the whole of the stannous oxide, and is converted into an orange-yellow compound of anomalous stannic acid with stannous oxide. (Fremy, *N. J. Pharm.* 1, 344.) According to Fremy's statement, the composition of this substance is probably $SnO,3SnO^2$.

B. Stannic Oxide. Stannic Acid. SnO^2.

Binoxide of Tin, Peroxide of Tin, Zinnoxyd, Zinnsäure, Deutoxyde d'Etain, Oxyde stannique, Acide stannique.—Found native in the form of *Tin-stone* and *Wood-tin.*

Formation. Tin, when heated in the air to its boiling point, burns with a bright white flame, and is converted into stannic oxide: *Flowers of Tin, Zinnblumen, Flores Stanni s. Jovis.* When fused in the air, it

becomes covered with a grey film, and is converted into a grey mixture of metallic tin and stannic oxide—*Tin-ash*—which, by longer ignition, is converted into pure stannic oxide.—Tin immersed in water containing $\frac{1}{800}$ part of potash, becomes dull, and imparts a small quantity of stannic oxide to the liquid. (A. Vogel, *J. pr. Chem.* 14, 107.)—2. Stannic oxide is formed in the decomposition of aqueous vapour by red-hot tin. (Gay-Lussac, Regnault.)—3. By nitric acid tin is converted rapidly, and with violent evolution of heat, into hydrated stannic acid, nitrate of ammonia being at the same time produced. Proust states that the oxidation of melted tin by fuming nitric acid produces explosion.—4. With heated oil of vitriol tin produces sulphurous acid and stannic sulphate.—5. The deflagration of tin with nitre produces stannate of potash.—6. When tin is heated with mercuric oxide, stannic oxide and metallic mercury are formed.—7. Stannous oxide remains unaltered in dry air at ordinary temperatures; in damp air, it is converted, in the course of a year, into stannic oxide. (Proust.) When heated in the air, or when merely touched by a spark from the flint and steel, it burns like tinder, with great rapidity, and produces a small quantity of white smoke. Hydrated stannous oxide likewise burns in the flame of a candle, but less rapidly. (Berzelius.)—Hydrated stannous oxide placed in contact with carbonate of copper under water, liberates carbonic acid and forms a mixture of stannic oxide and crystalline laminæ of copper. (Proust.)

Preparation. 1. By rapid or slow combustion of tin.—2. By precipitating the hydrate from hydrochlorate of stannic oxide by means of ammonia or carbonate of potash, and then washing and igniting.—3. By oxidating tin with nitric acid and igniting the hydrate after washing.—4. By heating 1 part of tin-filings in a retort with 4 parts of mercuric oxide. (Berzelius.)

Properties. Tin-stone belongs to the square prismatic system; Fig. 21, 29, 30, and other forms. $e:e' = 133^\circ\ 36'\ 18''$; $e:e'' = 67^\circ\ 42'\ 32''$. Cleavage parallel to *e*. (Hauy.)—Specific gravity 6·639 (Herapath), 6·96. (Mohs.) Harder than felspar; transparent, brownish-yellow. Often coloured black by ferric and manganic oxide.—The oxide prepared by method (1) is white; all the other artificial varieties are straw-yellow powders which redden litmus, and, when heated, acquire a transient orange-yellow and brown tint. Specific gravity of the artificial oxide—6·90 (Boullay); of that prepared by (3), 6·64 (Berzelius). Stannic oxide in all its forms is very refractory, and not volatile.

			Proust.	J. Davy.	Thomson.
Sn	59	78·67	78·1 — 78·4	78·34	78·38
2O	16	21·33	21·9 — 21·6	21·66	21·62
SnO^2	75	100·00	100·0 — 100·0	100·00	100·00

	Gay-Lussac.	Berzelius.	Klaproth.
Sn	78·6	78·62	79·5
2O	21·4	20·38	20·5
SnO^2	100·0	100·00	100·0

$SnO^2 = 735·29 + 2 \,.\, 100 = 935·29$. (Berzelius.)

Decompositions. By potassium and sodium with the aid of gentle heat, stannic oxide is reduced to the metallic state, the reduction being attended with incandescence.—It is also reduced to the metallic state by

charcoal at a strong red heat (also before the blowpipe on charcoal, if carbonate of soda be added and the flame strongly urged); likewise by carbonic oxide gas (Despretz, *Ann. Chim. Phys.* 43, 222; Leplay & Laurent, *Ann. Chim. Phys.* 65, 404; Gmelin); also by a mixture of equal volumes of carbonic oxide and carbonic acid gases (Leplay & Laurent); —by the oxy-hydrogen blowpipe (Clark, Pfaff), and by a current of hydrogen gas at the temperature at which tin decomposes water (Despretz);—easily at a low red heat by cyanide of potassium, which is thereby converted into cyanate of potash. (Liebig.)—By sulphur it is converted into bisulphide of tin, with evolution of sulphurous acid.

Combinations. Stannic acid exists—as discovered by Berzelius—in two isomeric states, and, accordingly, forms two series of compounds with water, acids, and bases. The hydrate obtained by the action of nitric acid upon tin contains the acid $a\mathrm{SnO^2}$, which combines with the smaller quantity of base, and is, therefore, analogous to metaphosphoric acid :—*b*. The hydrate obtained by precipitating bichloride of tin with an alkaline carbonate contains the acid $b\mathrm{SnO^2}$, which saturates three times as much base as the former, and is, therefore, analogous to ordinary phosphoric acid.—Berzelius calls the former of these modifications, *Oxydum stannicum*, and the latter *Oxydum parastannicum;* Fremy distinguishes the former as *Acide stannique*, and the latter as *Acide metastannique*. It would, however, be better to reverse these denominations, so as to make them agree with those of the modifications of phosphoric acid.*—For the present, the acid obtained by the action of nitric acid upon the metal may be distinguished by the epithet *Anomalous*.—¶ H. Rose is of opinion that there exist other modifications of stannic oxide besides those distinguished by Berzelius: in particular, he mentions *Tin-stone*, and the ignited oxide, with which the product obtained by heating stannic oxide to redness with alkaline carbonates, is probably identical. Rose is moreover inclined to regard the difference between the oxides *a* and *b* as due, not to any difference of saturating power which they may possess as acids, but to some other cause. (*Pogg.* 75, 1.) ¶

a. With Water. — *α. Anomalous Hydrate of Stannic Acid.*—Formed by completely oxidizing tin with moderately strong nitric acid, and washing the resulting white powder with water, till the liquid which runs through no longer reddens litmus-paper.—It is a white powder, which has a density of 4·933, and reddens litmus, even when thoroughly washed, although when ignited, it gives off nothing but pure water, without any nitric acid or nitrogen gas. (Berzelius.)—The hydrate dries up at 55°, in the form of colourless, translucent, friable lumps, having a conchoidal fracture. When dried at ordinary temperatures, it is white and opaque, with a silky lustre, and contains twice as much water as when dried at the higher temperature. (Thomson, *Ann. Phil.* 10, 149.)

					Berzelius.		Thomson. *Dried at* 55°.
$a\mathrm{SnO^2}$	75	....	89·29	.....	89	.....	80·64
HO	9	....	10·71	.....	11	.....	19·36
$\mathrm{HO},a\mathrm{SnO^2}$	84	....	100·00	.....	100	.....	100·00

¶ According to Fremy (*N. Ann. Chim. Phys.* 23, 393), the anomalous hydrate of stannic acid [hydrate of metastannic acid] dried at ordinary temperatures in air free from moisture, consists of $\mathrm{Sn^5O^{10}}+10\mathrm{HO}$; when

* In Fremy's later memoirs (e.g. *N. Ann. Chim. Phys.* 23, 393) this change is actually made.

dried in vacuo, it contains $Sn^5O^{10}+5HO$; when kept for several hours at 130°, it is reduced to $Sn^5O^{10}+4HO$; and at 160° it gives off another atom of water and becomes $Sn^5O^{10}+3HO$. The most permanent of these hydrates is that which contains 5HO. [The composition per cent. of this hydrate is the same as that of the ordinary hydrate of stannic acid dried in vacuo, SnO^2,HO.] (*Comp.* Schaffner, *Ann. Pharm.* 56, 174.)—On dissolving any of the above-mentioned hydrates in caustic potash, and precipitating by an acid, a precipitate of stannic acid (*metastannic acid*) is obtained, insoluble in nitric acid, but soluble in ammonia. ¶

β. Ordinary Hydrate of Stannic Acid. 1. By precipitating hydrochlorate of stannic oxide with carbonate of lime, not in excess. The washed precipitate reddens litmus. (Fremy, *N. J. Pharm.* 1, 342; also *Pogg.* 55, 519). If carbonate of potash is used as the precipitant instead of carbonate of lime, the precipitate obtained consists of stannate of potash, which, under these circumstances, is insoluble in water. (Fremy.) —2. By precipitating with a caustic alkali and washing thoroughly. The gelatinous precipitate resembles pieces of glass when dry; it reddens moistened litmus-paper, and is slightly soluble in water. (Berzelius.) —The ordinary hydrate of stannic acid contains more water than the anomalous hydrate, and, when boiled in water, or dried for some time in vacuo over oil of vitriol at ordinary temperatures, gives off water, and is converted into the anomalous hydrate. (Graham, *Ann. Pharm.* 13, 146.) According to Fremy, also, this hydrate contains more water than the anomalous hydrate, and is converted into the latter by drying at a strong heat. [Fremy's later results have already been given, *vid. sup.*]

b. With Acids, forming the SALTS OF STANNIC OXIDE, or STANNIC SALTS.—The native oxide, and likewise the artificial oxide after ignition, are quite incapable of combining with acids. By ignition with excess of caustic or carbonated potash or soda, the oxide is rendered soluble in acids.

α. Anomalous Stannic Salts.—The anomalous hydrate of stannic acid does not dissolve in acids, but takes up some of them, *e. g.* sulphuric and hydrochloric acid, in small quantity. When the compound thus formed with sulphuric acid is digested in water, after the excess of acid has been removed by decantation, it gives up to the water the acid which it has taken up; the hydrochloric acid compound dissolves in water, but is precipitated from the solution by acids. (Berzelius.) [vid. *Anomalous Hydrochlorate of Stannic Oxide.*]—¶ The solutions obtained in the manner just described are decomposed by boiling, the stannic oxide being completely precipitated, and the more quickly in proportion as the quantity of free acid in the solution is less.—Caustic potash or soda added to the solution throws down a white precipitate of the hydrated oxide, soluble in a moderate excess of the re-agent, but re-precipitated on the addition of a larger quantity. The precipitate thus formed disappears on the addition of water; according to Weber, it contains, when dried at 100°, $KO,Sn^7O^{14}+3HO$.—Ammonia gives a white precipitate insoluble in excess; the addition of tartaric acid does not prevent the precipitation. —Carbonate of potash also gives a white precipitate, insoluble in excess. —A solution of αSnO^2, in the smallest possible quantity of hydrochloric acid, gives no precipitate with phosphoric acid, but a copious white precipitate, in the course of 12 hours, with arsenic acid.—Nitrate of silver gives a white precipitate, from which ammonia dissolves out chloride of silver and leaves a residue of stannic oxide.—Tincture of galls gives,

after a few hours, a whitish-yellow precipitate.—Sulphuric acid, added to a solution of αSnO^2 in hydrochloric acid—even if the hydrochloric acid is in considerable excess—produces a copious precipitate, consisting of stannic oxide and sulphuric acid, the latter of which may be extracted by water. The precipitate, if heated with hydrochlorate or nitric acid, dissolves on the addition of water. The solution, when left to itself for a while, deposits a copious precipitate. ¶

β. Ordinary Stannic Salts. These salts are obtained: 1. By exposing stannous salts to the air, or treating them with chlorine, or heating them with nitric acid, care being taken not to use too much. Since 1 atom of stannous oxide requires but 1 atom of acid to form a normal salt, whereas 1 atom of stannic oxide requires 2 atoms of acid (II. 6), it follows that if a normal stannous salt is to be converted into a normal stannic salt by the action of the air or of nitric acid, it must first be mixed with a quantity of acid equal to that which it already contains; in default of the requisite quantity of acid, a precipitate is formed during the oxidation, consisting either of hydrated stannic oxide or of a basic salt.—2. By dissolving the ordinary hydrate of stannic oxide in acids.—3. When any specimen of stannic oxide, natural or artificial—previously ignited with potash, and thereby rendered soluble—is treated with acids [a potash-salt is, however, formed at the same time].—Stannic salts are colourless or yellowish. Those which are soluble in water redden litmus strongly, and have a sour, metallic, and styptic taste. Those which contain a volatile acid readily give it off when ignited. Before the blowpipe they behave like stannous salts. When boiled with nitric acid, they deposit the anomalous hydrate of stannic oxide, or a salt of that base. According to H. Rose, the same result is produced on boiling a solution largely diluted with water.—Zinc and cadmium immersed in solutions of stannic salts, precipitate the tin in the dendritic form. Iron precipitates the tin only under the circumstances mentioned under the head of *stannous salts;* lead ceases to act as soon as it becomes covered with a coating of metallic tin. (Fischer.)—Hydrosulphuric acid throws down from these solutions, even when they contain excess of acid, a yellow precipitate of hydrated bisulphide of tin: the precipitate is formed immediately on boiling; but at ordinary temperatures, and in dilute solutions, it takes some time to form. The same precipitate is formed by hydrosulphate of ammonia. It is soluble in hydrosulphate of ammonia, caustic ammonia, caustic potash, and carbonate of potash; the solution in caustic potash or carbonate of potash deposits hydrated stannic oxide after a while. (H. Rose.)—Ammonia throws down a white bulky hydrate, which dissolves, with some turbidity, in a very large excess of ammonia; the solution becomes clear after standing for some time, but subsequently deposits a copious precipitate. (Rose.) The precipitate dissolves readily if the solution of the tin-salt is dilute—imperfectly, if it is concentrated. (Gm.) Tartaric acid prevents the precipitation by ammonia. (H. Rose.)—Potash throws down a white bulky hydrate [containing potash ?], easily soluble in a slight excess of the alkali.—Monocarbonate of potash precipitates the hydrate [stannate of potash, according to Fremy] with some degree of effervescence; the precipitate dissolves in excess of the re-agent, but separates again completely after standing for a while. The hydrate precipitated by sesquicarbonate of ammonia and bicarbonate of potash does not dissolve in excess of those re-agents. (H. Rose.)—Carbonate of baryta, strontia, lime, and magnesia precipitate the salts of stannic oxide, even in the cold (Demarçay); the hydrate thereby precipitated is free from

alkali. (Fremy.) Phosphate of soda throws down white phosphate of stannic oxide. ¶. When phosphoric acid (aPO^5) is mixed with hydrochlorate of stannic oxide, the mixture solidifies, in the course of a few days, to a colourless jelly: arsenious acid gives, after a while, a somewhat copious precipitate. ¶.—Tincture of galls shows no action at first, but the mixture, after a while, solidifies in a gelatinous mass. (H. Rose.) Succinate of ammonia precipitates stannic salts completely. (Gahn & Berzelius.)—Ferrocyanide of potassium produces a white turbidity after some time; subsequently the mixture solidifies to a stiff jelly, insoluble in hydrochloric acid: the greater the degree of dilution, the more slowly does the solidification take place. (H. Rose.) When hydrochlorate of stannic oxide is boiled with acetate of soda or formiate of potash, a precipitate is formed, which re-dissolves on cooling, or when washed with cold water. (Liebig.)—Phosphuretted hydrogen gas gives no precipitate with hydrochlorate of stannic oxide, but colours it yellow. (H. Rose.) Iodide of potassium, chloride of gold, oxalic acid, sulphuric, nitric, hydrochloric, and arsenic acid, and ferrocyanide of potassium, give no precipitate. ¶. If the solution be very largely diluted with water, sulphuric acid produces a slight precipitate, which, however, is soluble in hydrochloric acid. Nitrate of silver in excess gives a precipitate perfectly soluble in ammonia. ¶.—Those stannic salts which are insoluble in water, dissolve—provided they have not been ignited—in hydrochloric acid, but not in sal-ammoniac.

c. With Salifiable Bases, forming salts called STANNATES.

α. *Anomalous Stannates.* By dissolving the anomalous hydrate in aqueous alkalis. These salts are composed of 3 At. stannic acid, with 1 At. metallic oxide, $=MO,3SnO^2$, and contain water as an essential constituent, by virtue of which the stannic oxide acquires the character of an acid; hence, when the salts are heated, the stannic oxide is separated in the anhydrous state. By ignition with an alkali, the anomalous stannates are converted into ordinary stannates. (Fremy.) Acids added to the solution of the hydrate in aqueous caustic alkalis, or alkaline carbonates, precipitate the hydrate in the anomalous state; consequently, the precipitate is not soluble in excess of the acid. (Berzelius.)

β. *Ordinary Stannates.* 1. By dissolving the ordinary hydrate of stannic acid in aqueous alkalis.—2. By fusing the anhydrous acid, or either of its hydrates, in a silver crucible, with caustic potash or carbonate of potash.—3. The stannates of the earthy alkalis, earths and heavy metallic oxides, are obtained by precipitating the soluble salts of these bases with the stannate of potash obtained by either of the preceding methods. (Berzelius.) The ordinary stannates contain at most 1 atom of base to 1 atom of acid, $=MO,SnO^2$. (Moberg, *Berz. Jahresber.* 22, 142; also *J. pr. Chem.* 28, 230; Fremy.) The stannates of the fixed alkalis, if they do not contain excess of alkali, are resolved, by ignition, into anhydrous stannic acid, and a compound of a small quantity of stannic acid with the whole of the alkali. Acids—even carbonic acid—decompose them, throwing down the ordinary hydrate of stannic acid. (Berzelius.)

According to Kastner (*Kast. Arch.* 19, 423) there exists a *Stannuretted Hydrogen gas.*

Carbonic acid does not combine with either of the oxides of tin. (Bergman, Proust.)

TIN AND BORON.

BORATE OF STANNOUS OXIDE.—Borax forms with hydrochlorate of stannous oxide, a white precipitate which fuses to a grey slag. (Wenzel.)

TIN AND PHOSPHORUS.

A. PHOSPHIDE OF TIN.—*a.* Formed by throwing phosphorus upon melted tin, or by fusing together equal parts of tin and glacial phosphoric acid, whereby phosphate of stannic or stannous oxide is likewise formed. (Pelletier, Landgrebe, *Schw.* 55, 106.) The compound may also be formed by heating in a blast-furnace for an hour: 6 parts of tin-filings or 8 of stannic oxide with 1 charcoal, 10 bone-ash, 5 pounded quartz, and 5 boracic acid. (Berthier, *Ann. Chim. Phys.* 33, 180.) Silver-white (lead-coloured: *Berthier*). May be cut with the knife; extends under the hammer, but at the same time splits into laminæ. Contains from 13 to 14 per cent. of phosphorus, which burns away on the application of heat. (Pelletier.) *b.* When the compound of bichloride of tin with phosphuretted hydrogen is decomposed by water, the phosphuretted hydrogen, as it escapes, reduces the bichloride of tin to the state of protochloride, and at the same time precipitates phosphide of tin in the form of a yellow powder, which remains for a long time suspended in the liquid, and oxidizes readily in the air. When washed and dried out of contact of air, it exhibits the phosphorus flame before the blowpipe. When ignited in hydrogen gas, it gives up its phosphorus, amounting to 55·43—56·88 per cent., and is converted into metallic tin. (H. Rose, *Pogg.* 24, 326.)

B. PHOSPHITE OF STANNOUS OXIDE, or STANNOUS PHOSPHITE.—Hydrochlorate of stannous oxide is precipitated by phosphite of ammonia, and the white precipitate washed till the wash-water, after boiling with nitric acid, no longer gives a turbidity with solution of silver. The salt, when heated in a retort, blackens without tumefaction, fuses without glowing, gives off hydrogen rich in phosphorus, and yields a sublimate of phosphorus. It is readily oxidized, with formation of a jelly, by warm nitric acid, and, on subsequent evaporation and ignition, yields 109·54 per cent. of stannic phosphate, containing 74·16 stannic oxide and 35·38 phosphoric acid. Its solution in hydrochloric acid exerts a powerful reducing action on several metals. (H. Rose, *Pogg.* 9, 45.)

					H. Rose.
2SnO	134·0	....	67·54	.....	66·24
PO^3	55·4	....	27·92	.....	27·44
HO	9·0	....	4·54	.....	6·32
$2SnO, PO^3 + Aq.$	198·4	....	100·00	.....	100·00

In consequence of the difficulty of drying the salt, the analysis gave too much water. (H. Rose.)

C. PHOSPHITE OF STANNIC OXIDE, or STANNIC PHOSPHITE.—The aqueous solution of bichloride of tin gives, with phosphite of ammonia, a white precipitate which dries up to a glassy, brittle mass. This, when heated, gives off merely water, without any gas, because the binoxide of tin is converted into protoxide: hence the residue is soluble in hydrochloric

and 3 sal-ammoniac;—*g.* 2 parts stannous oxide and 1 sulphur (Proust) [yields 2·4 mosaic gold];—*h.* 8 parts stannic oxide, 7 sulphur, and 4 sal-ammoniac (Woulfe);—*i.* 10 parts protosulphide of tin, 5 sulphur, and 4 sal-ammoniac (Woulfe);—*k.* 5 parts protosulphide of tin, 1 protochloride, and 2 sulphur (Woulfe);—*l.* 5 parts protosulphide of tin and 8 corrosive sublimate (Woulfe) [gives a very beautiful preparation];—*m.* Hydrated bisulphide of tin [obtained by deflagrating tin with nitre, dissolving the stannic oxide in hydrochloric acid, and precipitating with solution of liver of sulphur] (Van Mons).

Either of these mixtures or compounds is heated in a retort or a loosely-closed flask placed in the sand-bath, or in an inverted Passau crucible, having its mouth closed with a tile and its upturned base perforated with an aperture, which is covered with aludels. (Woulfe.) A gentle heat is first applied for some hours; afterwards the heat is raised, but not quite to redness.—The greater part of the mosaic gold is found at the bottom of the vessel—the smaller, but purer and finer portion, sublimes.

Properties.—Gold-coloured, translucent, delicate scales or six-sided laminæ, unctuous to the touch. Specific gravity 4·425 (P. Boullay); 4,600 (Karsten).

				J. Davy.	Berzelius.
Sn	59	64·84		63·6	65
2S	32	35·16		36·4	35
SnS^2	91	100·00		100·0	100

Decompositions. By ignition it is resolved into sulphur and protosulphide of tin, a portion of the bisulphide, however, subliming at the same time in a very beautiful form. If the action of the heat has not been long continued, protosulphide of tin is found at the bottom, above it a thin layer of sesquisulphide, and undecomposed mosaic gold at the top. (Berzelius.) The sulphurous acid gas observed by Proust, and previously also by Berzelius, is not evolved unless air has access to the heated substance. (Gay-Lussac, Berzelius.)—2. Boiling aqua-regia converts it into sulphuric acid and stannic oxide. Hydrochloric acid or nitric acid alone has no action on it.—3. Deliquesces in chlorine gas at ordinary temperatures, forming a brown liquid, and afterwards solidifies in yellow crystals of $SnCl^2,2SCl^2$. (H. Rose.)—Mosaic gold dissolves in a heated solution of potash [also in carbonate of potash, with evolution of carbonic acid], forming stannate of potash and sulphostannate of potassium:

$$3SnS^2 + 3KO = KO,SnO^2 + 2(KS,SnS^2).$$

(For the decomposition by litharge, vid. *Lead-oxide.*)

Hydrated Bisulphide of Tin, or *Bi-hydrosulphate of Stannic Oxide.*—1. By precipitating hydrochlorate of stannic oxide with sulphuretted hydrogen or an alkaline hydrosulphate.—2. By precipitating aqueous sulphostannate of potassium with hydrochloric acid.—Light yellow, loosely-coherent flakes, which dry up to dark yellow, hard lumps, having a conchoidal fracture. When gently heated, it gives off water, sulphur, and sulphurous acid (?), and is reduced to mosaic gold. (Proust.) At a higher temperature, it gives off the rest of its water with violent decrepitation, and is at the same time reduced to sesquisulphide by the loss of ½ At. sulphur; or at a still higher temperature, to protosulphide. (Ber-

zelius.) Dissolves in boiling hydrochloric acid with evolution of sulphuretted hydrogen, and is thereby converted into hydrochlorate of stannic-oxide. (Proust.)

Bisulphide of tin unites with the more basic metallic sulphides, forming salts called *Sulphostannates.* These compounds are obtained: 1. By dissolving either the anhydrous or the hydrated bisulphide of tin in aqueous alkaline hydrosulphates or caustic alkalis. The hydrated sulphide dissolves more readily than the anhydrous; with the latter, a boiling heat is required, to insure complete saturation. If the alkaline hydrosulphates contain 2 atoms of hydrosulphuric acid, 1 atom of the latter is expelled with effervescence. When caustic alkalis are used, the resulting solution likewise contains stannate of potash. (*vid. sup.*)—2. By precipitating a heavy metallic salt with aqueous sulphostannate of potassium. Those sulphostannates which contain an alkali-metal are not decomposed by ignition in close vessels.

D. Tetrathionate of Stannous Oxide.—Tetrathionic acid gives a white precipitate with hydrochlorate of stannous oxide. (Fordos and Gélis.)

E. *Hyposulphite of Stannous oxide?*—Aqueous sulphurous acid and metallic tin produce protosulphide of tin in the form of a black powder, and a solution of stannous hyposulphite, from which acids evolve sulphurous acid and precipitate sulphur. (Fourcroy & Vauquelin.) According to Berzelius, and likewise according to Fordos & Gélis, this process yields but very little hyposulphite of stannous-oxide, together with the sulphide, but on the other hand, a large quantity of sulphite,—the tin, in fact, behaving exactly like cadmium under similar circumstances (p. 57).

F. Sulphite of Stannous Oxide, or Stannous Sulphite.—Sulphite of ammonia added to hydrochlorate of stannous oxide throws down, at ordinary temperatures, the greater part, and at a boiling heat, the whole of the stannous oxide, in the form of a white basic salt. This salt gradually gives up all its acid to boiling water, and is converted into pale yellow, anhydrous protoxide of tin. (Berthier, *N. Ann. Chim. Phys.* 7, 81; *Comp.* Böttinger, *Ann. Pharm.* 51, 408.)

¶ G. Stannous Hyposulphate.—Known only in solution. When concentrated in vacuo, it deposits protosulphide of tin. (Bouquet.) ¶

H. Sulphate of Stannous Oxide, or Stannous Sulphate.—*a. Basic.*—Precipitated on mixing *b* with an alkali. (A. Berthollet.)

b. Monosulphate.—1. Protosulphide of tin heated with red oxide of mercury yields the anhydrous salt, which bears a dull red heat without decomposition.—2. By heating tin in oil of vitriol slightly diluted.—3. By dissolving hydrated stannous oxide in sulphuric acid.—4. Sulphuric acid added to solution of hydrochlorate of stannous oxide throws down a white powder. The liquid obtained by (3), and the solution of the saline mass (1), (2), or of the white powder (4), all yield needles on cooling. (A. Berthollet.) At a red heat the salt is resolved into sulphurous acid, oxygen gas, and stannic oxide. (Gay-Lussac.) When ignited in hydrogen gas, it leaves metallic tin with a small quantity of sulphide. (Arfvedson, *Pogg.* 1, 74.) ¶ According to Bouquet (*N. J. Pharm.* 11, 459), the salt

SnO, SO^3 crystallizes in laminæ from a hot saturated solution of recently precipitated stannous oxide in dilute sulphuric acid. It is very soluble in water; the solution soon becomes turbid from deposition of a basic salt, but its transparency is restored by adding a few drops of sulphuric acid. When ignited it leaves stannic oxide. Combines with the sulphates of potash and ammonia, forming crystallizable compounds. ¶

I. Sulphate of Stannic Oxide, or Stannic Sulphate.—*a. Ordinary.* 1. By dissolving ordinary hydrate of stannic oxide in aqueous sulphuric acid.—2. By heating tin with excess of oil of vitriol, whereupon sulphurous acid and sulphur are given off, and stannic sulphate remains behind. Kraskowitz (*Pogg.* 35, 518) heats 1 part of granulated tin with 3 parts of oil of vitriol in a capacious iron vessel; whereupon slight effervescence is at first produced, with formation of a white scum; then suddenly great heat is developed, and sulphurous acid mixed with sulphur vapour is given off; the vessel should therefore be cooled to prevent frothing over. After the frothing has ceased, the excess of oil of vitriol is driven off by the application of a stronger heat, which is continued till the residue becomes friable, and thereby separable from the metallic tin mixed with it. The aqueous solution (1) yields no precipitate on boiling. (Berzelius.)

b. Anomalous. The oxide of tin produced by the action of nitric acid does not dissolve in sulphuric acid either concentrated or dilute; a portion of the acid is, however, absorbed by it, with tumefaction, and may be extracted by water. (Berzelius.)

K. Sulphocarbonate of Stannous Sulphide, and Sulphocarbonate of Stannic Sulphide.—Aqueous sulphocarbonate of calcium gives a dark brown precipitate with stannous salts and brownish-yellow with stannic salts. (Berzelius.)

Tin and Selenium.

A. Selenide of Tin.—*a.* Tin combines with selenium, on the application of heat, forming a grey, metallic, shining substance, which, when heated in the air, is readily decomposed without fusion, yielding selenium which volatilizes, and stannic oxide which remains behind.—*b. Biselenide of Tin* may be obtained by precipitating hydrochlorate of stannic oxide with hydroselenic acid.

B. Selenite of Stannic Oxide.—White powder, insoluble in water, but soluble in hydrochloric acid, and precipitated from the solution on the addition of water. When heated, it first gives off water, and then the whole of its acid. (Berzelius.) Formula of the dry salt, $SnO^2, 2SeO^2$. (Muspratt.)

Tin and Iodine.

A. Protiodide of Tin, or Stannous Iodide.—*Iodostannous Acid.* 1. When tin-filings are heated with a twofold quantity of iodine, a brown-red, translucent compound is formed, which yields a dingy orange-yellow powder, and fuses very easily (according to Sir H. Davy, it volatilizes when heated more strongly); the combination is attended with

noise and ignition. (Gay-Lussac, Rammelsberg, *Pogg*, 48, 169.) ¶ According to Henry (*Phil. Trans.* 1845, 363), tin heated with twice its weight of iodine, yields two compounds, the protiodide SnI, and the biniodide SnI^2, which may be separated by sublimation, the latter volatilizing at 180° C. while the former remains fixed at a red heat. ¶ 2. A dilute solution of protochloride of tin mixed with a very slight excess of iodide of potassium soon deposits a large quantity of yellowish-red crystalline tufts. If the mixture was warm, the iodide of tin is deposited, on cooling, in fine yellowish-red needles. (Boullay, *Ann. Chim. Phys.* 34, 372.) Gay-Lussac likewise obtained orange-yellow silky crystals, by treating the iodide of tin (1) with a small quantity of water, and pouring off the liquid from the separated hydrate of stannous oxide—that liquid containing stannous oxide with excess of hydriodic acid. According to Gay-Lussac, these crystals consist of acid hydriodate of stannous oxide, but, according to Boullay's analysis, they are formed of protiodide of tin.

Protiodide of tin, when heated in the air in contact with stannic oxide, leaves a substance, which, when treated with water, is resolved into stannic oxide and hydriodic acid which dissolves. (Boullay.) The iodide prepared by (1) is easily decomposed by water—especially with the aid of heat, and the more completely in proportion as the quantity of water is greater—yielding hydrated stannous oxide which is precipitated, and aqueous hydriodic acid containing a trace of tin. (Gay-Lussac, Rammelsberg.) ¶ Dissolves in water sparingly, but without decomposition; fuses readily and forms a dark-red mass, having a crystalline texture; yields a powder of a red colour and considerable lustre, like red lead. (Henry.) ¶ The iodide (2) dissolves in water without decomposition, and more abundantly in warm than in cold water; it is likewise soluble in hydrochlorate of stannous oxide. Hence it is not precipitated from a solution of that compound by small quantities of iodide of potassium. (Boullay.) Iodide of tin combines with the more basic metallic iodides. (Boullay.)

					Boullay (2.)
Sn	59	....	31·89	.....	32·01
I	126	....	68·11	.....	67·99
SnI	185	....	100·00	.....	100·00

When tin is heated in excess with iodine and a large quantity of water, violent action ensues, the tin is rapidly oxidated, and a solution of hydriodic acid is formed, containing but a trace of tin. (Gay-Lussac.)

On dissolving in aqueous iodide of potassium half as much iodine as it already contains, and adding protochloride of tin to the solution, the colourless mixture yields no precipitate, but on evaporation deposits a yellow powder, slightly soluble in water, probably Sn^2I^3. (Boullay.)

¶ B. Biniodide of Tin.—SnI^2.—1. Separated by sublimation from the mixture of protiodide and biniodide obtained by heating tin with twice its weight of iodine (*supra*).—2. By boiling equal parts of protochloride of tin and iodine with a small quantity of water. By (1): orange-yellow, shining crystals; by (2): red crystals. Sublimes at 180°. Easily decomposed by water. (Henry.) ¶

C and D. Stannous and Stannic Iodates.—Iodic acid and iodate of potash give white precipitates both with hydrochlorate of stannous oxide

and with hydrochlorate of stannic oxide. (Pleischl.) When hydrochlorate of stannous oxide is dropped into iodate of soda, iodate of stannous oxide is precipitated, white at first, but turning brown in a few minutes, and then grey, from liberation of iodine and formation of stannic hydrochlorate. If, on the contrary, the iodate of soda be added to the stannous hydrochlorate, the white precipitate which forms at first is quickly re-dissolved, and the solution acquires a yellow colour; with a larger quantity of iodate of soda, a separation of iodine takes place. (Rammelsberg, *Pogg.* 44, 567.)

Tin and Bromine.

A. Protobromide of Tin, or Stannous Bromide.—*Bromostannous Acid.*—Formed by heating tin in hydrobromic acid gas (Balard), or with protobromide of mercury (Löwig).—Greyish-white, with considerable lustre; when heated, it fuses to a yellowish oil.—When heated in the air or in contact with nitre, it gives off bibromide of tin and leaves the binoxide.

Aqueous Protobromide of Tin, or *Hydrobromate of Stannous Oxide.*—1. By dissolving stannous bromide in water.—2. Tin dissolves in aqueous hydrobromic acid with evolution of hydrogen, very slowly when the liquid is cold, more quickly when it is raised to the boiling point.—The colourless solution, which reddens litmus, becomes gelatinous when evaporated, but does not crystallize; when more strongly heated, it gives off hydrobromic acid. (Löwig.)

B. Bibromide of Tin, or Stannic Bromide.—*Bromostannic Acid.*—Tin takes fire in contact with bromine and is converted into stannic bromide. (Balard.)—2. Protobromide of tin with bromine yields the same compound. (Löwig.)—White, crystalline, easily fusible and volatile; gives off a faint white cloud when exposed to the air. In heated oil of vitriol, it fuses, without visible decomposition, into oily drops. With nitric acid, after a few seconds, it gives off bright-coloured vapours of bromine. Dissolves in water without apparent decomposition. (Balard.)

Bromine-water converts stannous oxide, with evolution of heat, into mono-hydrobromate of stannic oxide; on stannic oxide, bromine exerts no action. (Balard.)

C. Bromate of Stannous Oxide, or Stannous Bromate.—Bromate of potash gives a yellowish-white precipitate with hydrochlorate of stannous oxide. (Simon, *Repert.* 65, 207.)

D. Bromate of Stannic Oxide, or Stannic Bromate.—Aqueous bromic acid dissolves but a small quantity of the ordinary hydrate of stannic acid, even after digestion for weeks. The hydrate separated from the liquid becomes translucent and glassy when dried over oil and vitriol, and loses 18 per cent. when heated to 180°. (Rammelsberg, *Pogg.* 55, 87.)

Tin and Chlorine.

Protochloride of Tin, or Stannous Chloride.—*Chlorostannous Acid.*—*Butter of Tin.*—1. By gradually heating tin or amalgam of tin with calomel, or with at most two parts of corrosive sublimate, the mercury

volatilizing.—2. By heating tin in hydrochloric acid gas, hydrogen being set free.—3. By heating hydrochlorate of stannous oxide in close vessels —whereupon, when the heat is gradually raised to redness and the receiver changed, the chloride of tin passes over after the water. Capitaine (*J. Pharm.* 25, 552) gently heats commercial *tin-salt* in a capacious crucible (to prevent frothing over) as long as it froths up and gives off water and sulphuric acid—pours the mass, as soon as it is brought to a state of tranquil fusion, into a small crucible—then pounds it up coarsely, and distils it from a coated glass retort. The first portions of stannous chloride which pass over are perfectly pure; the last portions contain a small quantity of iron, from which they may be freed by a second distillation.

Translucent, almost pure white (frequently grey), with a fatty lustre and conchoidal fracture. Fuses at 250° to an oily liquid which penetrates the crucibles and makes them crack; boils at a heat near redness, but always with some degree of decomposition. (J. Davy, *Schw.* 10, 321; Capitaine.) When cooled after fusion, it remains liquid for a long time, but afterwards becomes syrupy and solidifies. (Marx.)

					J. Davy.
Sn	59·0	....	62·5	.....	62·22
Cl	35·4	....	37·5	.....	37·78
SnCl	94·4	....	100·0	.....	100·00

When heated to bright redness, it gives off bichloride of tin and afterwards unaltered protochloride, leaving a black shining mass which dissolves in aqueous hydrochloric acid with evolution of hydrogen gas, and forms a solution of stannous hydrochlorate. (A. Vogel, *Schw.* 21, 66.) When heated to the boiling point, it passes over in company with bichloride of tin, and leaves yellow, earthy stannous oxychloride, SnCl, SnO. (Capitaine.)—When heated with sulphur, it yields bichloride and bisulphide of tin. (Proust.)

$$2SnCl + 2S = SnCl^2 + SnS^2.$$

When heated in the air, or with nitre, chlorate of potash, or mercuric oxide, it gives off bichloride of tin and leaves binoxide.—At ordinary temperatures, it does not suffer much alteration by exposure to the air; in the course of three weeks, however, it becomes somewhat disintegrated, but still dissolves completely in water.

Hydrated and Aqueous Protochloride of Tin, or Crystallized and Aqueous Mono-hydrochlorate of Stannous Oxide.—Tin-salt.—1. Protochloride of tin dissolves without turbidity in water [freed from air?]. (Capitaine.) The solution is commonly turbid, partly perhaps from the presence of air in the water, partly because the chloride of tin may have been mixed with oxychloride.—2. Tin dissolves very slowly in cold, more quickly in warm hydrochloric acid, and with evolution of hydrogen gas. The preparation on the large scale is performed in copper vessels, which, so long as any portion of tin remains undissolved, are not attacked by the acid.—3. If granulated tin be covered with hydrochloric acid, then the acid poured off, and the tin exposed to the air—afterwards the acid poured on again, and so on alternately—the tin takes up oxygen from the air, whereby it becomes heated, and dissolves much more quickly than by the simple action of the acid. (Berard.)—¶ 4. In the preparation of *Tin-salt* on the large scale, Nöllner recommends that the hydrochloric acid, as it is evolved from the retorts, be made to act

directly upon granulated tin contained in stone-ware receivers adapted to the retorts, and that the concentrated solution of tin-salt thus formed be afterwards evaporated in tinned pans with the addition of granulated tin. (*Arch. Pharm.* 63, 120.)—¶ The solution, when evaporated and cooled, yields large, transparent, and colourless prisms (and octohedrons: *Dumas*), having a disagreeable metallic taste. According to Berzelius, their composition is SnCl,HO; according to Henry, they contain 2 atoms of water, SnCl,2HO. The crystals when heated evolve water and hydrochloric acid containing a small quantity of tin, and leave protochloride and protoxide of tin. Cold oil of vitriol separates from them but a small quantity of hydrochloric acid; heated oil of vitriol separates hydrochloric acid—together with small quantities of stannous chloride, sulphurous acid, and sulphuretted hydrogen [the two latter substances partly decomposing each other and yielding a precipitate of sulphur]—and forms stannic sulphate. (A. Vogel.)

The crystals generally give a turbid solution with water, which, however, may be rendered transparent by the addition of hydrochloric acid [partly, perhaps, because the crystals have become oxidated by exposure to the air, partly because the air contains water]. The turbidity of the solution increases with excess of water, and diminishes with excess of the tin-salt. (Fischer.)—The solution absorbs oxygen from the air, and if it does not contain an excess of hydrochloric acid, becomes turbid, from formation of bi-hydrochlorate of stannic oxide and precipitation of stannous oxychloride. Probably in this manner:

$$3(SnO,HCl) + O = SnO^2,2HCl + SnCl,SnO + HO.$$

By longer exposure to the air, the solution recovers its transparency and acquires a yellow colour—the change being slower as the solution is more concentrated. (Fischer, *Kastn. Arch.* 13, 225; Capitaine.) [Does there exist a mono-hydrochlorate of stannic oxide, which forms a yellow solution in water?]—The solution of stannous hydrochlorate mixed with sulphurous acid, becomes yellow and turbid, especially when warmed, and yields a deep-yellow precipitate of hydrated bisulphide of tin, the odour of sulphurous acid being at the same time destroyed, and hydrochlorate of stannic oxide formed. (Hering, *Ann. Pharm.* 29, 90.) Probably thus:

$$6SnO + 2SO^2 = 5SnO^2 + SnS^2.$$

The stannic oxide formed remains dissolved in the excess of hydrochloric acid.—According to Girardin (*Ann. Chim. Phys.* 61, 286), if the hydrochloric acid contains even a small quantity of sulphurous acid, the solution of the tin-salt in it is attended with the formation of a yellow cloudiness; and if water be afterwards added, a faint smell of sulphuretted hydrogen is evolved and a yellowish-brown precipitate formed, which is a mixture of stannic sulphide and stannic oxide.—Trithionic acid added to the heated tin-solution throws down sulphide of tin. (Persoz.)—The solution reduces hypochlorous acid, evolving chlorine and being itself converted into a stannic salt. (Balard.) It likewise reduces nitric acid to nitric oxide, and this again, by longer contact, to nitrous oxide;—tungstic acid, even when united with an alkali, to blue oxide of tungsten;—molybdic acid to blue oxide of molybdenum;—chromic acid to chromic oxide;—manganic acid to manganous oxide;—hydrated peroxide of manganese, on boiling, to manganous oxide, with precipitation of sesquioxide of tin (Fuchs);—arsenic acid to arsenious acid, and this, by longer digestion, to metallic arsenic (Woulfe, *Crell. Chem. J.* 1, 155);—antimonious acid to

antimony (Woulfe);—mononitrate of bismuth-oxide to black suboxide (A. Vogel);—the red and brown peroxides of lead to chloride of lead (A. Vogel);—ferric salts to ferrous salts (with formation of hydrochlorate of sesquioxide-of-tin, (Fuchs, *comp.* p. 80);—cupric oxide and its salts to dichloride of copper;—the protoxide, dichloride, protochloride, and cyanide of mercury to metallic mercury (A. Vogel, *Kastn. Arch.* 23, 78); —silver-salts to metallic silver;—with gold-salts, the stannous solution forms a precipitate which is brown or purple according to circumstances. —Copper immersed in the stannous solution mixed with a large quantity of hydrochloric acid, throws down metallic tin in the form of a greyish-black powder, only however when the solution is exposed to the air and boiled. (Reinsch, *J. pr. Chem.* 24, 248.)

Protochloride of tin unites with the chlorides of the alkali-metals, forming salts which may be called *Chlorostannites.*—According to Kuhlmann, it forms definite compounds with nitrous, hyponitric, and nitric acid. It is easily soluble in absolute alcohol. (Capitaine.)

B. Hydrated Stannous Oxychloride, or Di-hydrochlorate of Stannous Oxide.—By precipitating hydrochlorate of stannous oxide with an insufficient quantity of potash.—White powder. (Proust.)—At a red heat, it yields water containing hydrochloric acid and hydrochlorate of stannous oxide, a sublimate of protochloride of tin and a residue of stannous oxide.—Froths up violently with strong nitric acid; gives off hydrochloric acid gas when treated with oil of vitriol; and dissolves without effervescence in hydrochloric acid, acetic acid, and dilute nitric or sulphuric acid, forming stannous salts. (J. Davy, *Schw.* 10, 325.)

				Or:				J. Davy.
SnCl	94·4	....	50·11	2SnO	134·0	....	71·13	.... 70·4
SnO	67·0	....	35·56	HCl	36·4	....	19·32	
3HO	27·0	....	14·33	2HO	18·0	....	9·55	
SnCl, SnO + 3Aq.	188·4	....	100·00		188·4	....	100·00	

C. Aqueous Sesquichloride of Tin, or Hydrochlorate of Sesquioxide-of-tin.—Hydrated sesquioxide of tin dissolves readily in hydrochloric acid. (Fuchs.) It dissolves with difficulty in cold dilute hydrochloric acid, and the concentrated acid does not become saturated with it till after long digestion, which, to prevent oxidation, must be performed in close vessels. The solution has a purely astringent taste, yields, with hydrosulphuric acid, a lighter brown precipitate than the stannous-salt, and a remarkably fine purple with gold-salts. (Fuchs.)

D. Bichloride of Tin, or Stannic Chloride.—*Chlorostannic Acid.* —*Fuming Spirit of Libavius, Spiritus fumans Libavii.*

Formation. 1. Tin-foil takes fire after a while in chlorine gas, and burns with emission of red sparks, forming bichloride of tin.—2. Protochloride of tin likewise takes fire in chlorine gas at ordinary temperatures.—3. Tin heated with protochloride of mercury volatilizes in the form of bichloride. 4. Protosulphide of tin heated with sulphur or with oxidized bodies is converted into bisulphide.

Preparation. 1. When dry chlorine gas is slowly passed through the retort *d*, *App.* 52, containing tin-foil or melted tin, the bichloride distils over into the receiver *e*, which must be kept cool.—2. By distilling 1 part of tin with 5 parts of protochloride of mercury.—3. By distilling

concentrated hydrochlorate of stannic oxide with fuming oil of vitriol. (J. Davy.)—4. By distilling common salt with stannic sulphate:

$$2NaCl + SnO^2,2SO^3 = 2(NaO,SO^3) + SnCl^2.$$

The stannic sulphate prepared by method 2, page 82, is pounded in a mortar while still warm—then sifted—intimately mixed with an equal weight of common salt—and heated in an iron retort with glass receiver (or in a glass retort—in which, however, it is difficult to effect complete decomposition)—the heat being gradually raised as long as anything passes over. The bichloride of tin which distils over—together with hydrochloric acid gas—contains chloride of iron and crystals of hydrated bichloride of tin. To free it from iron and water, it is rectified in a glass retort with from twice to four times its weight of oil of vitriol. (Von Kraskowitz. *Pogg.* 35, 518.)

Properties. Thin, colourless liquid, which does not freeze at —29°, boils at 120° under a pressure of 0·767 met., and yields a vapour whose density is 9·1997 (Dumas); gives off white fumes in the air at ordinary temperatures.

					Berzelius.		J. Davy.
Sn	59·0	....	45·45	....	54·43	....	42·1
2Cl	70·8	....	54·55	....	45·57	....	57·9
$SnCl^2$	129·9	....	100·00	....	100·00	....	100·0

	Vol.		Sp. gr.
Tin vapour	1	.....	4·0905
Chlorine gas	2	.....	4·9086
Vapour of $SnCl^2$	1	.....	8·9991

Decomposed by sulphuretted hydrogen with the aid of heat, the products being hydrochloric acid gas and bisulphide of tin. (H. Rose, *Pogg.* 24, 339.)

$$SnCl^2 + 2HS = SnS^2 + 2HCl.$$

When heated with nitric acid, it gives off chlorine and nitric oxide, and deposits stannic oxide. (Gay-Lussac.) To mercury it slowly gives up chlorine, so that calomel and stannous chloride are produced. (Dumas.)—Alcohol decomposes it, with formation of hydrochloric ether and deposition of stannous oxychloride. With oil of turpentine it becomes strongly heated, the turpentine sometimes taking fire, and deposits stannic oxide. (J. Davy.) Not decomposed by olefiant gas. (Wöhler.)

Hydrated Bichloride of Tin, or *Crystallized Hydrochlorate of Stannic Oxide.*—22 parts of bichloride of tin solidify with 7 parts of water, forming a colourless mass of crystals fusible by heat. (Adet.)—¶ If this crystalline mass be treated with an additional quantity of water, and the liquid gently evaporated, deliquescent crystals are obtained, which appear to contain 5 atoms of water: $SnCl^2,5HO$. When dried over sulphuric acid, they give off 3 At. water, and are converted into $SnCl^2,2HO$. (Lewy, *Compt. rend.* 21, 369.) ¶

Aqueous Bichloride of Tin, or *Aqueous Hydrochlorate of Stannic Oxide.*—*a. Ordinary.*—Colour-makers' *Composition.*—1. By dissolving bichloride of tin in water.—2. By saturating an aqueous solution of stannous chloride with chlorine gas.—3. By mixing the same solution with a quantity of hydrochloric acid twice as great as that which it already contains, and exposing it to the air for some time,—or by heating

it with nitric acid not in excess.—4. By dissolving tin in aqua-regia not containing too much nitric acid. A mixture of nitric acid with sal-ammoniac or common salt, or of hydrochloric acid with nitre may likewise be used.—The solution obtained by the agency of nitric acid always retains a portion of that acid, and therefore deposits anomalous hydrate of stannic oxide when boiled (Bolley, *Ann. Pharm.* 39, 103); according to H. Rose, this effect is not produced till the solution has attained a somewhat high degree of concentration.—The compound may likewise be obtained by dissolving ordinary hydrate of stannic oxide in hydrochloric acid. The anomalous hydrate of stannic oxide, when distilled with hydrochloric acid, is partly converted into ordinary hydrochlorate of stannic oxide, which passes over, while the rest remains behind, as anomalous hydrochlorate of stannic oxide, in the form of a yellow mass, which, when digested in water, partly dissolves and partly swells up. (Berzelius.)—Colourless liquid, not decomposible by boiling; yields crystals when evaporated and cooled.

b. Anomalous.—The hydrate of stannic oxide produced by the action of nitric acid does not dissolve in hydrochloric acid even when boiling and concentrated, but takes up a portion of that acid and acquires a yellowish tint, and is thereby converted—after the excess of acid has been poured off, and the residue dried on bibulous paper—into a soft yellow mass perfectly soluble in water. Nevertheless, the resulting solution, even when largely diluted, coagulates at a boiling heat, and if concentrated becomes as thick as white of egg. It likewise yields a precipitate when mixed with concentrated hydrochloric acid,—but the precipitate dissolves again in water, after the acid is poured off. When this compound is distilled, aqueous hydrochloric acid passes over first, then hydrochloric acid gas, with a small quantity of stannic chloride, while anhydrous stannic oxide is left behind. (Berzelius.)—Ammonia or potash added to the aqueous solution yields a white precipitate slightly soluble in excess of the alkali. (H. Rose.)

E. and F.—Bichloride of tin dissolves sulphur and phosphorus, forming oily liquids.

G. Chlorostannate of Phosphuretted Hydrogen.—Bichloride of tin absorbs both the more inflammable and the less inflammable phosphuretted hydrogen gas without decomposition, thereby acquiring a yellow colour, and being subsequently converted into a yellow solid body which fumes in the air and absorbs moisture with avidity. When heated out of contact of air, it gives off hydrochloric acid gas with a sublimate of phosphorus, and leaves protochloride of tin:

$$PH^3, 3SnCl^2 = 3SnCl + 3HCl + P.$$

Ammoniacal gas colours the compound black, even in the cold, and appears to form ammonio-bichloride of tin together with several other products.—Water added to this compound gives off non-spontaneously inflammable phosphuretted hydrogen gas with effervescence, and forms hydrochlorate of stannous and of stannic oxide, together with a precipitate of terphosphide of tin (p. 88). Aqueous solution of potash, carbonate of ammonia, or carbonate of potash, and hydrochloric acid likewise give rise to the evolution of the less inflammable variety of phosphuretted hydrogen; but aqueous ammonia evolves the spontaneously inflammable gas. (H. Rose, *Pogg.* 24, 159.)

					H. Rose.
PH^3	34·4		8·12		8·64
$3SnCl^2$	389·4		91·88		91·36
$PH^3,3SnCl^2$	423·8		100·00		100·00

H.—Bichloride of tin may be mixed with terchloride of phosphorus.

I. Chlorosulphide of Tin.—$SnS^2,2SnCl^2$.—Sulphuretted hydrogen is rapidly absorbed by bichloride of tin, with formation of hydrochloric acid gas:

$$3SnCl^2 + 2HS = SnS^2,2SnCl^2 + 2HCl.$$

The liquid obtained by perfect saturation with sulphuretted hydrogen is transparent, of a yellowish or reddish colour, and heavier than water. When heated, it leaves bisulphide of tin, while the bichloride volatilizes. Water added to the liquid dissolves out the latter compound and throws down 25·07 per cent. of bisulphide of tin. (Dumas, *J. Chim. Méd.* 8, 478; also *Schw.* 66, 409.)

K. Chloride of Sulphur and Tin.—Produced by the action of chlorine gas on bisulphide of tin at ordinary temperatures:

$$SnS^2 + 6Cl = SnCl^2 + 2SCl^2.$$

A bulb is blown on a glass tube and filled with mosaic gold; a cylindrical enlargement is also blown on the tube, the end drawn out, and passed into a chloride of calcium tube, to keep out the moisture of the air. As soon as the dried chlorine gas passed into the bulb has decomposed the mosaic gold, the bulb is gently heated till the compound sublimes into the cylindrical enlargement; air is passed over it to drive out the excess of chlorine; and the cylinder sealed at both ends. Protosulphide of tin likewise yields this compound, mixed however with free bichloride (p. 78).

Large yellow crystals, which fuse when heated, and sublime without decomposition; they fume in the air more strongly than bichloride of tin.—The crystals dissolve gradually but completely in dilute nitric acid, with evolution of nitrous fumes; the solution contains stannic oxide, together with the whole of the sulphur in the form of sulphuric acid. With fuming nitric acid they form a thick white mass, perfectly soluble in water.—With water they form a solution which is milky from separated sulphur, but does not smell of sulphurous acid. The solution when boiled yields a deposit of stannic oxide soluble in hydrochloric acid; with hydrosulphuric acid it forms bisulphide of tin, and the filtered liquid treated with chloride of barium yields sulphate of baryta. With nitrate of silver-oxide, it yields a white curdy precipitate, which contains hyposulphite of silver-oxide, together with chloride of silver, and therefore turns black. Hence it appears that the aqueous solution contains bichloride of tin, sulphuric acid, hyposulphurous acid, and hydrochloric acid. [But whence the precipitation of stannic oxide on boiling?]—Aqueous ammonia separates sulphur and part of the stannic oxide from the crystals, but takes up a large proportion of the stannic oxide, together with hyposulphurous, sulphuric, and hydrochloric acid.—The crystals absorb ammoniacal gas with great evolution of heat, and are converted into a yellowish-brown mass; and when this mass is digested in water, the whole of the stannic oxide is left undissolved together with sulphur

in the form of white flakes. The filtrate, which is neutral at first, acquires after a while, the property of reddening litmus, and contains hyposulphite, sulphate, and hydrochlorate of ammonia. (H. Rose, *Pogg.* 42, 517.)

					H. Rose.
Sn	59·0	....	19·44	.....	19·82
2S	32·0	....	10·55	.....	11·38
6Cl	212·4	....	70·01	.....	68·19
$SnCl^2, 2SCl^3$	303·4	....	100·00	.....	99·39

Bichloride of tin may likewise be mixed with dichloride of sulphur, and forms crystals with it in the cold. (H. Rose, *Pogg.* 16, 67.)

I. Sulphate of Stannic Chloride.—Bichloride of tin absorbs the vapour of anhydrous sulphuric acid in large quantity, and without evolution of sulphurous acid, and when perfectly saturated with it, solidifies in a transparent and colourless mass. It dissolves clearly in a small quantity of water, with milky turbidity in a larger quantity.

On distilling this mass, a colourless syrup (*a*) passes over and hardens into a transparent, colourless, brittle mass; a white mealy sublimate *b* collects in the neck of the retort; and an unfused mass (*c*) remains in the retort.

a. The brittle mass forms with water a very turbid solution containing stannic oxide, hydrochloric acid, and sulphuric acid, with separation of white flakes mixed with heavy oily drops; these dissolve but slowly in water, as sulphate of terchloride-of-sulphur; the flakes which remain behind dissolve readily in hydrochloric, sulphuric, or nitric acid.

$$a = 6(SnCl^2, SnO^2) + 5(SCl^3, 5SO^3).$$

				Or:					H. Rose.
$6SnCl^2$	778·8	....	27·43	12Sn	708·0	....	24·93	....	25·07
$6SnO^2$	450·0	....	15·85	30S	480·0	....	16·90	....	17·40
$5SCl^3$	611·0	....	21·51	27Cl	955·8	....	33·66	....	33·96
$25SO^3$	1000·0	....	35·21	87O	696·0	....	24·51	....	
	2839·8	....	100·00		2839·8	....	100·00		

Sometimes the compound contains less ($SnCl^2$, SnO^2), and in that case it dissolves in water with little or no turbidity.

b. The mealy sublimate contains less quintosulphate of chloride-of-sulphur than *a*, and therefore forms no oil-drops or only a few, when put into water.

c. The residue in the retort, after being sufficiently heated, contains nothing but stannic oxide with sulphuric acid. The large quantity of stannic oxide arises from the simultaneous formation of terchloride of sulphur from the sulphur of the sulphuric acid. (H. Rose, *Pogg.* 44, 320.)

¶ M. Iodochloride of Tin.—SnCl, SnI.—When a concentrated solution of stannous chloride is boiled with iodine, a deposit of stannous iodide is formed, and the liquid, after filtration and cooling, yields straw-yellow, silky crystals of the iodochloride.—These crystals are decomposed by contact with water; they are not volatile. They contain 12·63 per cent. of chlorine, 45·86 iodine, and 42·16 tin. (Henry, *Phil. Trans.* 1845, 363.) ¶

Tin and Fluorine.

Hydrated Protofluoride of Tin, or Hydrofluate of Stannous Oxide.—Aqueous hydrofluoric acid, even when warmed, has no sensible action upon tin. The solution of stannous oxide in aqueous hydrofluoric acid, when evaporated out of contact of air, yields small, white, very brilliant crystals, which have a very sour taste, and are easily soluble in water. (Gay-Lussac & Thénard.)—Opaque prisms which taste first sweet and then bitter; and when exposed to the air, are readily converted by oxidation into SnF^2, SnO^2. (Berzelius, *Pogg.* 1, 34.) According to Unverdorben (*N. Tr.* 1, 36), hydrofluate of ammonia gives, with hydrochlorate of stannous oxide, a precipitate consisting of glimmering, metal-shining laminæ, soluble in dilute potash.

B. Aqueous Bifluoride of Tin, or Hydrofluate of Stannic Oxide.—Aqueous hydrofluoric acid forms with stannic oxide a solution, which, when evaporated, gives off hydrofluoric acid, and is converted into an insoluble (basic ?) salt. (Gay-Lussac & Thénard.) The solution when boiled coagulates like white of egg. (Berzelius.)

Tin and Nitrogen.

A. Nitrate of Stannous Oxide, or Stannous Nitrate.—1. Very dilute nitric acid, at ordinary temperatures, dissolves tin in the form of stannous oxide, the action being attended, not with evolution of nitrous gas, but with formation of ammonia. (Proust.)—2. By dissolving hydrated stannous oxide in dilute nitric acid, a salt is obtained not mixed with nitrate of ammonia. (Berzelius.)—3. By precipitating protochloride of tin with nitrate of lead, and filtering to separate the chloride of lead. The solution is less liable to change, if mixed with excess of nitrate of lead. (Fischer, *Schw.* 56, 360.)—Yellow solution, which if left to itself for some time, deposits a small portion of stannous oxide (gelatinous hydrate of stannous oxide, according to Berzelius), but if heated with fresh nitric acid, deposits the whole of the tin in the form of stannic oxide [anomalous hydrate of that oxide]. (Proust.)

B. Nitrate of Stannic Oxide, or Stannic Nitrate.—The ordinary hydrate of stannic oxide dissolves abundantly in nitric acid, and neutralizes it completely. The solution has a bitter taste. If the acid used is rather strong, a portion of the salt separates from it in silky crystals.—At 50°, it deposits nearly all the oxide in the hydrated state, in gelatinous lumps, which dry up to a transparent and colourless mass; the oxide thus obtained behaves like ordinary hydrate of stannic oxide, excepting that it will not again dissolve freely in nitric acid, unless it be previously treated with ammonia. If the solution contains nitrate of ammonia, it does not decompose at ordinary temperatures; if it does not contain that substance, and especially if it be much diluted, it deposits stannic oxide, which, however, disappears again on the addition of nitrate of ammonia. (Berzelius.)

The anomalous hydrate of stannic oxide is completely insoluble in nitric acid, even if previously digested in ammonia. (Berzelius.)

C. Nitric Oxide with Stannic Chloride.—Crystalline; easy to distil; decomposible by water. (Kuhlmann.)

Hydrated stannous oxide is nearly insoluble in aqueous ammonia. (Berzelius, *Pogg.* 28, 444.)—In a large quantity of carbonate of ammonia, it dissolves almost completely. (Wittstein, *Repert.* 63, 334.)

D. Stannate of Ammonia.—1. The ordinary hydrate of stannic acid dissolves in aqueous ammonia. The saturated solution evaporated over oil of vitriol in a receiver containing air leaves a yellowish jelly, containing $NH^4O,2SnO^2$, together with water. (Moberg.)—2. Aqueous stannate of potash precipitates stannate of ammonia from a solution of sal-ammoniac. The gelatinous precipitate dissolves in pure water, but is reprecipitated by ammonia. The aqueous solution, when spontaneously evaporated, becomes viscid, but does not lose its transparency. (Berzelius.) —The anomalous hydrate of stannic oxide does not dissolve in ammonia.

E. Sulphostannate of Ammonium.—By dissolving hydrated stannic oxide in aqueous bihydrosulphate of ammonia.—No stannate of ammonia is thereby produced. (Berzelius.)

F. Ammonio-protiodide of Tin.—100 parts of stannous iodide absorb 20·9 parts of ammonia, evolving heat, and forming a white compound. (Rammelsberg, *Pogg.* 48, 169.)

					Rammelsberg.
$2NH^3$	34	....	15·52	.....	17·29
SnI	185	....	84·48	.....	82·71
$2NH^3$, SnI	219	....	100·00	.....	100·00

G. Iodostannite of Ammonium.—By precipitating tolerably concentrated hydrochlorate of stannous oxide with hydriodate of ammonia.—Greenish-yellow needles, decomposed by water, with separation of red iodide of tin. (P. Boullay.)

	Dried.				Boullay.
NH^3, HI	144	....	28·01	.....	29·02
2SnI	370	....	71·99	.....	70·98
NH^4I, 2SnI	514	....	100·00	.....	100·00

H. Ammonio-protochloride of Tin.—2 At. protochloride of tin absorb, when heated, 1 At. ammoniacal gas. (Persoz.)

I. Ammonio-bichloride of Tin.—The fuming spirit of Libavius absorbs ammoniacal gas at ordinary temperatures, causing evolution of heat. (H. Davy.)—The solid mass, as it forms, must be assiduously pulverized, and again exposed to the ammoniacal gas, if we would ensure its complete saturation. (H. Rose.) The white mass may be sublimed without decomposition (even in hydrogen gas: *H. Rose*), and when heated in the air, evaporates in white pungent fumes. (H. Davy.) When dissolved in water it reddens litmus strongly. (Grouvelle.) After sublimation, it is crystalline and has a somewhat yellowish white tint. When heated with sodium, it emits a brilliant violet light, and is resolved into granules of tin, chloride of sodium, and ammoniacal gas. It dissolves completely in cold water (Grouvelle, H. Rose), only that which has not been sublimed forming a turbid solution. The solution, if evaporated in vacuo over oil of vitriol, leaves the unde-

composed compound in the form of a mass of crystals, which sublime without decomposition. But if the cold solution (which gives no turbidity with ammonia) be heated, or left to itself for a few days, it deposits a jelly. Sulphuric acid likewise gives a gelatinous precipitate, soluble in a larger quantity of water. The same character is exhibited by aqueous bichloride of tin, to which a small quantity of ammonia has been added. The compound is not altered by phosphuretted hydrogen gas in the cold; when heated, it gives off ammonia and turns red on the surface, probably from formation of a small quantity of chlorostannate of phosphuretted hydrogen. (H. Rose, *Pogg.* 24, 163.)

			H. Rose.		Persoz.	Grouvelle.
			sublimed.	*not sublimed.*		
NH^3	17·0	11·58	10·92	13·27	20·45	20·94
$SnCl^2$	129·8	88·42	89·08	86·73	79·55	79·06
$NH^3, SnCl^2$	146·8	100·00	100·00	100·00	100·00	100·00

The unsublimed compound yields a larger quantity of ammonia, because free ammonia adheres to it. (H. Rose.) According to Grouvelle and Persoz (*Ann. Chim. Phys.* 44, 322), the compound $=2NH^3,SnCl^2$.

K. Chlorostannite of Ammonium.—This is the residue obtained when tin-filings are heated with sal-ammoniac, ammonia and hydrogen gas being evolved; at a higher temperature it sublimes. (Proust, *N. Gehl.* 1, 249; Berzelius.) Regular octohedrons, which are permanent in the air, and redden litmus; their solution in water becomes turbid on boiling. (Apjohn.)

			Apjohn.
NH^4Cl	53·4	34·06	34·1
$SnCl$	94·4	60·20	60·3
HO	9·0	5·74	5·6
$NH^4Cl, SnCl + Aq.$	156·8	100·00	100·0

¶ Poggiale (*Compt. rend.* 20, 1180) has formed a compound containing $2NH^4Cl, SnCl + 3Aq$; it crystallizes in needles grouped in tufts, permanent in the air and decomposed by water. ¶

L. Chlorostannate of Ammonium.—*Pink Salt.*—1. Precipitated in the form of a white powder, on mixing concentrated solutions of bichloride of tin and sal-ammoniac. When a dilute mixture of the two solutions is slowly evaporated, the compound is deposited in small regular octohedrons and cubo-octohedrons. (Bolley, *Ann. Pharm.* 39, 100.) It may also be obtained by mixing a solution of 40 parts of tin in aqua-regia with 35 parts of sal-ammoniac at 100°, evaporating to dryness, dissolving the perfectly dried residue, which amounts to 120 parts, in water, and leaving the solution to crystallize. (Wittstein, *Repert.* 64, 7.)—2. Sublimes in transparent octohedrons during the preparation of mosaic gold with tin, sal-ammoniac, and sulphur, and may be purified by solution, filtration, and crystallization. (Gm.) The crystals decrepitate when heated, then evolve bichloride of tin, and afterwards sublime in white laminæ. (Wittstein.) Dissolves in 3 parts of water at 14·5°. The concentrated solution does not decompose on boiling; the dilute solution, when boiled, deposits the whole of the stannic oxide in white flakes. (Bolley.)

					Bolley.
NH^4	18·0	....	98·2	.....	9·9
Cl	35·4	....	19·33	.....	19·2
$SnCl^2$	129·8	....	70·85	.....	70·9
$NH^4Cl, SnCl^2$	183·2	....	100·00	.....	100·0

M. Hydrochlorate and Stannite of Ammonia.—By supersaturating aqueous protochloride of tin with ammonia till the precipitated stannous oxide is redissolved, and evaporating the solution in vacuo, this compound is obtained in crystals. (Berzelius.)

N. Nitrate of Stannic Oxide and Ammonia.—Nitrate of ammonia increases the solubility of stannic oxide in nitric acid; hence it is easier to dissolve tin without precipitation in nitric acid containing nitrate of ammonia. (Vid. *Nitrate of Stannic Oxide*, p. 92; also *Ann. Chim.* 42, 218.)

Tin and Potassium.

A. Alloy of Tin and Potassium.—*a.* Seven volumes of tin-filings unite with 2 volumes of potassium, with faint incandescence, and form an alloy, which is somewhat less white than tin, brittle, of fine-grained fracture, and easily fusible. Oxidizes quickly in the air, effervesces with water, and still more with aqueous acids.—*b.* With a larger quantity of potassium an alloy is obtained, which often, especially during pulverization, takes fire in the air. (Gay-Lussac & Thénard.)—*c.* When granulated tin is ignited with cream of tartar, or 100 parts of stannic oxide with 60 parts of tartar carbonized by roasting, and 8 parts of lamp-black (with 16 lamp-black a pyrophorus is formed), the tin takes up a small quantity of potassium, so that when thrown into water, it slowly evolves hydrogen gas. (Serullus, *Ann. Chim. Phys.* 21, 200.)

B. Stannite of Potash.—Hydrated stannous oxide dissolves readily in caustic potash. The solution is resolved, especially when heated, into crystallized tin and stannate of potash. (Proust.) Zinc separates the tin from it in soft laminæ. (Klaproth.) When solution of potash is completely saturated with hydrate of stannous oxide, and then left to evaporate in vacuo, the potash, at a certain degree of concentration, withdraws the water from the hydrated oxide, which thereupon becomes insoluble and falls to the bottom. (Fremy.)

C. Stannate of Potash.—*a. Ordinary.*—*α. Monostannate.*—1. By fusing stannic oxide or either of its hydrates with hydrate or carbonate of potash. If the fusion with carbonate of potash be interrupted before the carbonic acid is completely expelled, the same effect is produced as with titanic acid and carbonate of potash. (III. 484; II. Rose.) The fused mass generally contains an excess of potash.—2. By dissolving stannic oxide, or the ordinary or anomalous hydrate in hot, strong potash-ley. The solution saturated with hydrated stannic oxide and then evaporated in vacuo over oil of vitriol to a considerable degree of concentration, yields colourless, shining, oblique rhombic prisms, whose very acute lateral edges are often truncated; they have a caustic alkaline taste, do not deliquesce in the air, but absorb carbonic acid from it. Easily soluble in water whether hot or cold. (Moberg, *Berz. Jahresber.* 22, 142; *Ber. über d. Versamml. d. Naturf. in Prag.* 1837.) The

crystals turn red when heated, but do not melt. (Proust.) Lead immersed in the aqueous solution precipitates the whole of the tin. (Fischer, *Pogg.* 9, 263.) Copper in contact with tin is quickly tinned by the solution. (Böttger, *Ann. Pharm.* 39, 171.) Alcohol added to the solution precipitates the salt β.—¶ Ordinary stannate of potash does not lose its solubility in water by ignition; acids added to the solution of the ignited salt, throw down stannic acid, perfectly soluble in nitric acid. (Fremy.) ¶

	Anhydrous.				*Crystallized.*			Moberg.
KO	47·2	....	38·62	KO	47·2	....	31·64	31·88
SnO^2	75·0	....	61·38	SnO^2	75·0	....	50·27	49·00
				3HO	27·0	....	18·09	18·06
KO,SnO^2	122·2	....	100·00	+3Aq.	149·2	....	100·00	98·94

β. *Acid Salt.*—1. By precipitating the aqueous solution of *a* with alcohol.—2. When stannic salt is precipitated by carbonate of potash, hydrated stannic oxide containing potash is precipitated; and this, after the saline solution has been removed by decantation, dissolves in pure water, forming a milky liquid, which gives a precipitate with carbonate of potash. (Berzelius.)

b. Anomalous.—Fremy's Metastannate of Potash.—When the anomalous hydrate of stannic oxide is boiled with a very dilute solution of potash, a solution is formed, containing 16 parts of stannic oxide to 1 part of potash. The liquid, which appears bluish-white and opalescent by reflected, and deep yellow by transmitted light, becomes gelatinous on evaporation, and afterwards dries up to a deep yellow substance, which re-dissolves when treated with water. This substance is resolved by ignition into insoluble stannic oxide and a compound of potash with a small quantity of stannic oxide, which may be extracted by water. (Berzelius.) The anomalous hydrate dissolves imperfectly in aqueous potash, and, when the solution is left to itself for some time, partly separates out again. It does not dissolve in aqueous carbonate of potash. (H. Rose, *Anal. Chem.*) ¶ Fremy prepares metastannate of potash by dissolving metastannic acid (p. 73) in dilute potash-ley and adding solid caustic potash, whereupon the compound separates in the form of a white granular precipitate. This precipitate, when dried upon a porous porcelain plate, becomes resinous and translucent; it dissolves completely in water, forming an alkaline liquid which cannot be made to crystallize by evaporation, but on the addition of an acid, yields a precipitate of metastannic acid insoluble in nitric acid. Metastannate of potash, when heated with excess of caustic potash or left in contact with it for several days, is converted into stannate of potash. By ignition it is dehydrated and decomposed. From the ignited salt, water extracts potash and only a small quantity of metastannic acid; 100 parts of the salt, after ignition and treatment with water, yield 79 parts of metastannic acid. Fremy assigns to this salt the formula $KO,Sn^5O^{10}+4HO$. (*N. Ann. Chim. Phys.* 23, 393.) ¶

D. Sulphostannate of Potassium.—KS,SnS^2.—By dissolving anhydrous or hydrated bisulphide of tin in hydrosulphate of potash. If the bihydrosulphate be used, the second atom of hydrosulphuric acid is given off with effervescence; if the sulphide of tin is anhydrous, a boiling heat is required to insure saturation. Caustic potash with bisulphide of tin yields the same solution, likewise, however, containing stannate of potash.

$$3SnS^2 + 3KO = 2(KS, SnS^2) + KO, SnO^2.$$

Pale yellow liquid. When digested with excess of hydrated bisulphide of tin, it converts the latter into sesquisulphide, tin being deposited and sulphur dissolved, and a solution of polysulphide of potassium formed. Acids added to the solution of sulphostannate of potassium evolve hydrosulphuric acid and precipitate bisulphide of tin:

$$KS, SnS^2 + HO + SO^3 = KO, SO^3 + SnS^2 + HS.$$

For every 2·12 parts of bisulphide of tin (in the anhydrous state) which hydrochloric acid throws down from the liquid, there are formed 1·63 parts of chloride of potassium. Alcohol added to the yellow solution throws down a more concentrated solution of the same compound, in the form of a light yellow thickish liquid. (Berzelius.)

E. Iodostannite of Potassium.—Concentrated solutions of protochloride of tin and iodide of potassium solidify when mixed, in consequence of the formation of yellowish silky needles; the same may be obtained, but in a finer state of crystallization, from a solution in hot alcohol. When chlorine gas is passed over the anhydrous salt, the tin burns with emission of light and forms bichloride of tin, leaving a residue of chloride of potassium. A small quantity of water withdraws iodide of potassium from the salt; the remaining iodide dissolves on the addition of more water. The compound dissolves in hot alcohol, leaving but a small quantity of iodide of tin behind, and the solution yields crystals on cooling. (P. Boullay.)

				Or:				Boullay.
K	39·2	....	7·33	KI	165·2	....	30·87	33·76
2Sn	118·0	....	22·05	2SnI	370·0	....	69·13	66·24
3I	378·0	....	70·62					
KI, 2SnI	535·2	....	100·00		535·2	....	100·00	100·00

F. Chlorostannite of Potassium.—2KCl,SnCl + 3HO. Needles. (Poggiale.)

G. Chlorostannate of Potassium.—By evaporating aqueous bichloride of tin with chloride of potassium. Jacquelain (*Ann. Chim. Phys.* 66, 130) dissolves equal numbers of atoms of chloride of potassium and bichloride of tin in water. Wittstein (*Repert.* 64, 7) adds 5 parts of chloride of potassium to a solution of 4 parts of tin in aqua-regia, or fuses 1 At. anomalous hydrate of stannic oxide in a silver crucible with 1 At. hydrate of potash, and dissolves in hydrochloric acid. Bolley (*Ann. Pharm.* 39, 100) mixes dilute hydrochlorate of stannic oxide with excess of chloride of potassium.—Regular octohedrons (Bolley, Wittstein); rhombohedrons (Jacquelain). The crystals, which are permanent in the air, decrepitate when heated, give off bichloride of tin, and leave chloride of potassium mixed with a small quantity of stannic oxide (Bolley), or chloride (Wittstein).

					Jacquelain.	Or:				Bolley.
K	39·2	....	19·18	....	19·42	KCl	74·6	....	36·5	.... 36·3
Sn	59·0	....	28·86	....	28·67	$SnCl^2$	129·8	....	63·5	.... 63·7
3Cl	106·2	....	51·96	....	51·85					
KCl, $SnCl^2$	204·4	....	100·00	....	99·94		204·4	....	100·0	.... 100·0

H. Hydrochlorate and Stannite of Potash.—The liquid obtained by supersaturating hydrochlorate of stannous oxide with potash till the precipitate is re-dissolved, yields crystals when evaporated in vacuo. (Berzelius.)

Tin and Sodium.

A. Alloy of Tin and Sodium.—Four volumes of tin-filings unite with 1 volume of sodium at the melting point of tin—the combination being attended with evolution of light and heat—and form a white, very brittle, fine-grained alloy, which oxidizes in the air, and effervesces with water and with aqueous acids. (Gay-Lussac & Thénard.) The alloy may likewise be formed by igniting tin with charred soap. (Serullus.)

B. Stannite of Soda.—Hydrated stannous oxide dissolves in aqueous solution of soda.

C. Stannate of Soda.—*a. Ordinary.*—Solution of soda saturated with ordinary hydrate of stannic oxide yields—though not without difficulty—six-sided tabular crystals, which are lighter than the potash-salt and soluble in water. (Moberg.)

Anhydrous.		*Crystallized.*			Moberg.
NaO	31·2	NaO	31·2	23·42	23·5
SnO^2	75·0	SnO^2	75·0	56·31	56·0
		3HO	27·0	20·27	20·2
NaO,SnO^2	106·2	+3Aq	133·2	100·00	99·7

If hydrochlorate of stannous oxide be precipitated at a temperature above 40° with excess of carbonate of soda, the filtrate, on cooling, deposits a compound, which effervesces with acids after being washed, and is therefore probably a carbonate of stannous oxide and soda. (Leykauf, *J. pr. Chem.* 21, 317.)—¶. *b. Metastannate.*—Obtained by the action of concentrated soda-ley on metastannic acid. The salt is very difficultly soluble in water, white, granular, and crystalline. It is resolved at 60° (or at a boiling heat, if in solution) into metastannic acid and soda. Its composition appears to be : $NaO,Sn^5O^{10}+4Aq$. (Fremy.) ¶.

D. Sulphostannate of Sodium.—Similar to the potassium-compound. (Berzelius.)

E. Iodostannite of Sodium.—When a solution of iodide of sodium in concentrated hydrochlorate of stannous oxide is left to stand for some hours, it first deposits iodide of tin, and then pale yellow crystals of the iodostannite, decomposible by water. (P. Boullay.)

F. Chlorostannate of Sodium.—By evaporating a mixture of bichloride of tin and common salt. According to Wittstein, 1 part of common salt with 1 part of tin dissolved in aqua-regia; or 1 At. anomalous hydrate of stannic oxide fused with 1 At. hydrate of soda, and dissolved in hydrochloric acid. Anhydrous, deliquescent cubes, which, when ignited, leave common salt with a small quantity of chloride of tin. (Wittstein.) Rhombic laminæ, which are permanent in cold air, effloresce in warm air, give off 12 or 13 per cent. of water at 100, and the chloride of tin at

a red heat. (Bolley.) It remains to be determined by analysis, whether the salts obtained by Wittstein and by Bolley differ in anything besides their quantity of water. Lewy has formed a compound containing $NaCl,SnCl^2+5$ Aq.

G. Hydrochlorate and Stannite of Soda.—Analogous to the potash-compound. Delicate needles. (Berzelius.)

Tin and Barium.

By heating tin to whiteness with baryta, strontia or lime, and charcoal, Gay-Lussac and Thénard did not succeed in forming alloys of tin with the metals of these alkalis.

A. Stannate of Baryta.—Precipitated on mixing baryta-water or a baryta-salt with aqueous stannate of potash. The precipitate produced by baryta-water contains 20·9 (1 At.) baryta to 79·1 (4 At.) stannic acid. (Berzelius.) Moberg, by precipitating chloride of barium with stannate of potash, obtained a heavy white powder $=BaO,SnO^2+6$ Aq.

B. Sulphostannate of Barium.—Sulphostannate of potassium forms with baryta-salts, a light yellow precipitate soluble in water. (Berzelius.)

C. Iodostannite of Barium.—By dissolving stannous iodide in aqueous iodide of barium. Very soluble salt. (P. Boullay.)

¶. D. Chlorostannite of Barium.—$BaCl,SnCl+4$ Aq. Prepared by Poggiale.

E. Chlorostannate of Barium.—$BaCl,SnCl^2+5$ Aq. Prepared by Lewy. ¶.

F. Hydrochlorate and Stannite of Baryta.—Analogous to the potash-compound.

Tin and Strontium.

A. Stannate of Strontia.—By precipitating stannate of potash with strontia-water or a strontia-salt.

B. Sulphostannate of Strontium.—As with barium.

C. Iodostannite of Strontium.—As with barium.

¶. D. Chlorostannite of Strontium. — $SrCl,SnCl+4$ Aq.—Prepared by Poggiale.

E. Chlorostannate of Strontium.—$SrCl,SnCl^2+5$ Aq.—Prepared by Lewy. ¶.

F. Hydrochlorate and Stannite of Strontia.—Analogous to the potash-compound. Delicate needles. (Berzelius.)

Tin and Calcium.

A. Stannate of Lime.—Slowly precipitated when a lime-salt is mixed with stannate of potash. Contains $CaO,SnO^2 + 4$ Aq. (Moberg.)

B. Sulphostannate of Calcium.—Analogous to the barium compound.

Tin and Magnesium.

A. Stannate of Magnesia.—Stannate of potash precipitates from magnesia-salts a magma, which stops up the filter and cannot be washed. (Moberg.)

¶. B. Chlorostannate of Magnesium.—$MgCl,SnCl^2 + 5$ Aq. Prepared by Lewy. ¶.

C. Hydrochlorate and Stannite of Magnesia.—Similar to the potash-salt. Deliquescent.

Tin and Silicium.

A. Silicide of Tin.—Tin fuses with silicium before the blowpipe, forming a ductile alloy, which, when dissolved in acids, leaves a small quantity of silica. (Berzelius, *Pogg.* 1, 220.)

Quadrosilicate of soda precipitates bichloride of tin, but not the protochloride. (Walcker.)

B. Silico-fluoride of Tin.—Long prisms, very easily soluble in water. On evaporating the solution in the air, the stannous oxide is converted into stannic oxide, and is precipitated in combination with silica. (Berzelius.) According to Berzelius (*Pogg.* 1, 200), this salt contains protofluoride of tin; according to Berzelius's *Lehrbuch* (4, 532), on the contrary (writing the formula in accordance with the numbers adopted in this *Hand-book*), it is SnF^2,SiF^2.

Tin and Tungsten.

A. Tungstate of Stannous Oxide, or Stannous Tungstate.—Monotungstate of potash added to hydrochlorate of stannous oxide throws down a yellow powder, which gives off water and turns brown when heated, and bakes together at a red heat. Hydrochloric acid extracts from the powder the stannous oxide, which then converts the separated tungstic acid into blue oxide. The salt dissolves in oxalic acid and in potash, slowly in boiling phosphoric acid, and not at all in water. (Anthon, *J. pr. Chem.* 9, 341.)

	Ignited.		Anthon.		*Unignited.*		Anthon.
SnO	67	35·83	35·9	SnO	67	27·8	28
WO^3	120	64·17	64·1	WO^3	120	49·8	50
				6HO	54	22·4	22
SnO,WO^3	187	100·00	100·0	+ 6Aq.	241	100·0	100

B. STANNOUS SULPHOTUNGSTATE. — SnS,WS^3.—Voluminous brown flakes. (Berzelius.)

C. STANNIC SULPHOTUNGSTATE.—SnS^2,WS^3.—Greyish-yellow flakes. (Berzelius.)

TIN AND MOLYBDENUM.

A. MOLYBDATE OF STANNIC OXIDE, or STANNIC MOLYBDATE.—Grey powder, insoluble in water, but soluble in dilute hydrochloric acid with a blue, in concentrated hydrochloric acid with a green, and in aqueous potash with a brown colour; not altered by nitric acid. (Berzelius.) The blue precipitate, obtained by mixing an alkaline molybdate with stannous hydrochlorate, or by placing tin in contact with molybdic acid, water, and a very small quantity of hydrochloric acid—Richter's *Blue Carmine*, which was regarded by Bucholz as a molybdanite of stannic oxide—is, according to Berzelius, nothing more than a mixture of stannic molybdate and blue oxide of molybdenum.

B. STANNOUS SULPHOMOLYBDATE.—Formed by precipitating a stannous salt. Black precipitate.

C. STANNIC SULPHOMOLYBDATE. — By precipitating a stannic salt. The translucent brown precipitate becomes brownish-grey on drying.

D. STANNOUS PERSULPHOMOLYBDATE. — Hydrochlorate of stannous oxide is completely precipitated by an aqueous solution of the potassium-salt. The dark brown precipitate, when immersed in the liquid and exposed to the air, is converted into E, and dissolves gradually, forming a red solution.

E. STANNIC PERSULPHOMOLYBDATE.—Red precipitate, slightly soluble in water, in which it forms a red solution; hence, when it is precipitated, a portion remains dissolved. (Berzelius, *Pogg.* 7, 287.)

Alkaline *Vanadiates* give no precipitates with tin-salts. The yellow mixture of vanadiate of ammonia with hydrochlorate of stannous oxide loses its colour after a while; the mixture of vanadiate of ammonia with hydrochlorate of stannic oxide remains yellow. (Berzelius.)

TIN AND CHROMIUM.

A. *Stannate of Chromic Oxide?—a.* By heating chromate of stannic oxide to bright redness, a dark violet mass is obtained, which communicates to glazings a variety of tints, from rose-red to violet. (Leykauf, *J. pr. Chem.* 19, 127.) — *b. Hyper-acid Salt.* — *Mineral lac, Laque minérale.* 50 parts of stannic oxide very strongly ignited with 1 part of chromic oxide, yield a mass consisting of fine crystals and vitreous globules, of beautiful and very durable colour.—*c. Hyperacid Salt containing Stannate of Lime.* — *Pink-colour.* — 100 parts of stannic oxide are strongly ignited for some hours with 34 parts of chalk and from 1 to 1½ pt. chromic oxide, or 3 to 4 chromate of potash (perhaps also with the addition of 1 part silica and 1 part alumina). The dingy-red mass is washed with water containing hydrochloric acid, and thereby acquires a beautiful rose-red colour. It is soluble in rather strong hydro-

chloric acid, which is not the case with mineral lac; it is used to produce a red colour on *Fayence*. (Malaguti, *Ann. Chim. Phys.* 61, 433.)—*d. Hydrated?*—Monochromate of potash added to hydrochlorate of stannous oxide throws down a green mixture of chromic oxide and stannic oxide. (Grouvelle.)

B. Chromate of Stannous Oxide.—When hydrochlorate of stannous oxide is added to chromate of potash, the latter being in excess and the liquid agitated, chromate of stannous oxide is precipitated in yellow, curdy flocks. (Berzelius.) On the contrary, when dilute chromate of potash is added by small portions at a time, and with constant agitation, to hydrochlorate of stannous oxide, a greenish-white precipitate is produced, probably consisting of stannate of chromic oxide. If the tin-solution contains free acid, the whole remains dissolved, forming a green solution.

C. Chromate of Stannic Oxide.—Bi-hydrochlorate of stannic oxide, not containing any further excess of acid, forms a yellow precipitate with chromate of potash. The liquid above the precipitate acquires an orange-yellow colour, in consequence of the liberation of chromic acid. —The precipitate, after drying, is brownish-yellow and translucent; and is converted by ignition into violet-coloured stannate of chromic oxide.

Tin and Manganese.

Stannate of Manganous Oxide.—White powder, which gradually becomes dark brown by exposure to the air. (Berzelius.) According to Moberg, it acquires a yellow colour.

Permanganate of potash gives no precipitate with hydrochlorate of stannic oxide. (Fromherz.)

Tin and Arsenic.

A. Arsenide of Tin.—1. When pulverized arsenic is stirred about in melted tin, combination takes place, attended with evolution of light and heat. (Gehlen, A. Vogel.)—2. By heating tin with arsenious acid. (Gehlen.)—White, sonorous, and brittle, if the tin be not in too great excess; of laminar texture, and less fusible than tin.—Gives off its arsenic when fused in an open vessel. With hydrochloric acid it evolves arseniuretted hydrogen gas.—When it is dissolved in hydrochloric acid, there remains a black compound of tin with excess of arsenic, which gives off its arsenic when ignited, and then dissolves again in acids. An alloy containing excess of arsenic is not attacked by hydrochloric acid. (Soubeiran.)

B. *Arsenite of Stannic Oxide* or *Arseniate of Stannous Oxide?*—1. Arsenic acid with acetate of stannous oxide, or arseniate of potash with hydrochlorate of stannous oxide, forms a white precipitate, insoluble in water.—2. Tin dissolves in aqueous arsenic acid—arseniuretted hydrogen being evolved—and forms a gelatinous mass. (Scheele.)

C. Stannous Sulpharsenite.—By precipitating hydrochlorate of stannous oxide with a saturated solution of orpiment in hydrosulphate of

soda. The dark brown precipitate does not fuse when heated, but gives off part of its orpiment, and leaves a grey, metallic, porous mass.

D. STANNIC SULPHARSENITE.—The yellow, gummy precipitate obtained with hydrochlorate of stannic oxide, becomes orange-yellow on drying, yields a powder of a fine yellow colour, and behaves like C when heated. (Berzelius, *Pogg.* 7, 147.)

E. STANNOUS SULPHARSENIATE.—Both the bibasic and the terbasic sulpharsenite of sodium give dark chestnut-brown precipitates with hydrochlorate of stannous oxide.

F. STANNIC SULPHARSENIATE.—Both the bibasic and terbasic sodium-salts form, with hydrochlorate of stannic oxide, pale yellow, gummy precipitates, which stop up the filter, and become orange-yellow on drying. (Berzelius, *Pogg.* 7, 28.)

G. Bichloride of tin combines with terchloride of arsenic, the combination being attended with evolution of heat. (J. Davy.)

TIN AND ANTIMONY.

A. ANTIMONIDE OF TIN.—Formed by fusing the two metals together —in which case the combination takes place without evolution of light and heat—or by fusing sulphide of antimony with excess of tin.

a. 12 pts. tin to 1 antimony. The alloy called *Pewter*, used for making vessels to hold liquids.

b. 10 pts. tin to 1 antimony. Perfectly ductile. (Chaudet.)

c. 7 pts. tin to 1 antimony. Produces a fine tone. (Kastner, *Kastn. Arch.* 19, 324.)

d. 3 pts. tin to 1 antimony. Less ductile than tin; sp. gr. 7·059. (Chaudet.)

e. 1·5 pts. tin to 1 antimony. Brittle, less laminar than antimony. (Gehlen.)

f. 1 pt. tin to 1 antimony. Extremely brittle; easily pulverized; sp. gr. 6·803. (Chaudet.)

The ductile alloys are rendered brittle by the addition of a small quantity of lead. If the quantity of tin be not less than 9 times as great as that of the antimony, boiling hydrochloric acid extracts the whole of it (with evolution of antimoniuretted hydrogen?), and leaves the antimony in the form of a black powder. (Chaudet, *Ann. Chim. Phys.* 3, 376; also *N. Tr.* 2, 1, 167.)

B. ANTIMONIATE OF STANNIC OXIDE.—When hydrochloric acid in which antimonic acid and stannic oxide are dissolved together, is diluted with water, the two metallic acids are precipitated in combination, and the liquid loses nearly all the metal that it contained. (Thénard.)—If tin on the one hand, and antimony on the other, be heated with excess of nitric acid, till red fumes are no longer given off, and the two liquids be then mixed, the two white powders therein contained are converted into a yellow powder, with fresh evolution of nitrous vapours,—because the antimoniate of antimonic oxide [nitrate of antimonic oxide] formed from the antimony, becomes oxidized and converted into antimonic acid,

which then unites with the stannous oxide [stannic oxide]. (Levol, *N. Ann. Chim. Phys.* 1, 504; also *J. pr. Chem.* 24, 253.)

C. STANNOUS SULPHANTIMONIATE. — Schlippe's salt gives a dark brown precipitate with hydrochlorate of stannic oxide. (Rammelsberg.)

TIN AND TELLURIUM.

A. TELLURIDE OF TIN.—Tellurium fuses with tin.

B. STANNOUS SULPHOTELLURITE.—The brown precipitate turns black on drying, and, when heated in a retort, gives off sulphur, and is converted into a grey mass having the metallic lustre.

C. STANNIC SULPHOTELLURITE. — The precipitate is dark brown. (Berzelius.)

TIN AND BISMUTH.

A. ALLOYS OF TIN AND BISMUTH.—An alloy of 177 parts (3 At.) of tin and 213 parts (1 At.) of bismuth, when cooled from a state of fusion, exhibits but one solidifying point—inasmuch as it first cools regularly down to 143°, and then remains at that temperature for a considerable time, till the latent heat set free in the solidification of the alloy, has had time to escape. But all other alloys of these metals likewise exhibit a higher solidifying point (which may be distinguished as the *Point of Separation*), inasmuch as the excess of the one or the other metal [or rather—since the point is variable—another definite alloy containing an excess of one of the two metals] solidifies first, and afterwards, at 143°, the hitherto fluid alloy containing Sn^3Bi. The higher solidifying point, or point of separation, is 190° for Sn^8Bi, 160° for Sn^4Bi, 150° for Sn^2Bi, 170° for Sn^4Bi^3, and 190° for SnBi. (Rudberg, *Pogg.* 18, 240.)

a. 40 parts tin to 1 bismuth; perfectly ductile; the addition of 1 part of lead diminishes its extensibility.

b. 25 parts of tin to 1 bismuth. Slightly ductile. (Chaudet.)

c. 8 parts tin to 1 bismuth. Fuses at 199°. (Lewis.)

d. 3 parts tin to 1 bismuth. Pulverizable; of dull grey fracture, and specific gravity 7·776. Gives up all its tin with a small quantity of bismuth to heated hydrochloric acid. (Chaudet.)

e. 2 parts tin to 1 bismuth. Fuses at 166°. (Lewis.)

f. 236 parts (4 At.) tin to 213 parts (1 At.) bismuth. Sp. gr. 8·085. (Regnault.)

g. 1 part tin to 1 bismuth. Perfectly brittle; pulverizable; of fine-grained fracture; sp. gr. 8·345. (Chaudet.) Fuses at 138°. (Lewis.) Expands strongly in solidifying. (Marx.) With hydrochloric acid it behaves like *d.* (Chaudet, *Ann. Chim. Phys.* 5, 142; also *N. Tr.* 2, 2, 349.)

h. 177 pts. (3 At.) tin to 213 pts. (1 At.) bismuth. Fuses between 131° and 137°. (Dobereiner, *Kastn. Arch.* 3, 90.)

i. 118 pts. (2 At.) tin to 213 pts. (1 At.) bismuth. Sp. gr. 8·759. (Regnault.)

B. ALLOY OF ANTIMONY, BISMUTH, AND TIN.—236 parts (4 At.) tin to 213 pts. (1 At.) bismuth, and 129 pts (1 At.) antimony. Sp. gr. 7·883 at 20°. (Regnault, *Ann. Chim. Phys.* 76, 136.)

Tin and Zinc.

A. Alloys of Tin and Zinc.—These two metals fuse together with ease; the alloy is harder than either tin or zinc, and less extensible than tin. Sn^6Zn has but one solidifying point, viz., at 204°. (Compare the observations made with reference to *Bismuth and Tin.*) The other alloys exhibit in addition a higher solidifying point, which varies according to the nature of the alloy. (Rudberg.)

	$Sn^{12}Zn$	Sn^6Zn	Sn^4Zn	Sn^3Zn	Sn^2Zn	$SnZn$
Variable point	210°		230°	250°	280°	320°
Fixed point	204°	204°	204°	204°	204°	204°

B. Stannate of Zinc-oxide.—Stannate of potash yields ,with zinc-salts, a white precipitate composed of ZnO,SnO^2+2Aq. (Moberg.)

Other Compounds of Tin.

With Lead, Iron, Cobalt, Nickel, Copper, Mercury, Silver, Gold, Platinum, Palladium, and Iridium. As tin makes these metals brittle, it was called by the alchemists, *Diabolus Metallorum.*

Chapter XXXI.

LEAD.

Bucholz. Lead-oxide and its salts. *A. Gehl.* 5, 253.
Thomson. Oxides of lead. *A. Gehl.* 4, 92.
Berzelius. *Gilb.* 166 and 186; 46, 131. Further: *Schw.* 7, 71.
Winkelblech. Oxides of lead. *Ann. Pharm.* 21, 21; also *J. pr. Chem.* 10, 227.
Bromeis. On the salts produced by the action of lead on the nitrate of lead-oxide. *Ann. Pharm.* 72, 38.

Synonymes:—*Blei, Plomb, Plumbum, Saturnus.*

History.—Known from the earliest times.

Sources.—In the metallic state?—as red lead; as peroxide; as carbonate, phosphate, sulphate, selenite, tungstate, molybdate, vanadiate, chromate, and arseniate of lead-oxide; as aluminate of lead-oxide; as chloride of lead, sometimes united with oxide or carbonate; as selenide of lead; as sulphide of lead, either alone or associated with other metals, as

in Feather-ore, Zinkenite, Boulangerite, Plagionite, Jamesonite, Geocronite, Needle-ore, Kobellite, Bournonite, and Antimonial Copper-glance; as telluride of lead, sometimes associated with other metals, as in Foliated Tellurium and White Tellurium. Traces of lead have been found in sea-water (*N. Ann. Chim. Phys.* 28, 129); in coal (*Chem. Soc. Qu. J.* 2, 1); and in the blood of animals (*Jahresber. L. & K. I.*, 874).

Preparation on the large scale.—1. Native carbonate of lead, or artificially prepared lead-oxide, *e. g.* litharge, is fused in a smelting or a reverberatory furnace, in contact with charcoal, and often with the addition of lime.—2. Galena is freed from part of its sulphur by roasting, either in heaps, or on hearths, or in calcining furnaces, and the roasted ore, consisting of lead, lead-oxide, sulphate of lead-oxide, and undecomposed sulphide of lead, is fused in contact with charcoal, and generally with addition of lime, in a smelting or a reverberatory furnace —whereby metallic lead and slags are produced, and mixed with them, a quantity of undecomposed galena (*leadstone*), which is again roasted and fused. Or the unroasted galena is smelted in a furnace with iron, iron-cinder, or an ore of iron, whereby metallic lead, slags, and plumbiferous sulphide of iron are obtained; the latter is roasted and fused a second time.

The lead thus obtained from the ore, called *Pig-lead* (*Werkblei*), frequently contains gold and silver, to separate which it is oxidized on cupels, on which the gold and silver are left. The lead oxide thus obtained, called *Litharge* (*Bleiglätte*), is reduced as in (1)—the process is called the *Refining of Litharge* (*das Glätte-Frischen*)—and yields *Refined Lead.*

Purification.—1. Nitrate of lead-oxide purified by repeated crystallization is ignited in an earthen crucible to expel the nitric acid, and the resulting oxide reduced by charcoal.—2. Oxalate of lead-oxide ignited alone in a covered crucible yields lead free from charcoal. (Winkelblech.) 3. Solution of sugar-of-lead is precipitated by sulphuric acid (in which process the acetic acid may likewise be obtained from it), and the sulphate of lead-oxide, after thorough washing, is strongly ignited in a covered crucible with 2 At. charcoal (Berthier); 152 parts of lead-sulphate intimately mixed with 12 parts of charcoal powder. The same result may likewise be obtained by igniting at a lower temperature 8 parts of lead-sulphate with 4 parts of potash and 1 part of charcoal,—or, according to A. Werner (*J. pr. Chem.* 13, 191), 16 parts of lead-sulphate with 9 parts of Chili-saltpetre, 4 of resin, and 4 of charcoal powder, till the mass, after deflagration, yields no more bubbles.

Properties.—Crystallizes in regular octohedrons. Mongez obtained lead, by slow cooling, in four-sided pyramids; Braunsdorf (*J. pr. Chem.* 1, 120) obtained well-defined octohedrons; and Marx (*Schw.* 57, 193), by allowing a considerable quantity of melted lead to cool till half of it solidified, then making a hole in the crust and pouring out the still fluid portion, obtained it in fern-like forms similar to those in which sal-ammoniac crystallizes. Specific gravity 11·3305 (Kupffer); 11·352 (Brisson, Herepath); 11·358 (Morveau); 11·3888 (according to Karsten, when purified by method 1); 11·445, when in the utmost attainable state of purity (Berzelius). According to Morveau, the density of lead is rather diminished than increased by hammering, in consequence of the formation of cracks; if, however, the metal is prevented from expanding

on either side, its density increases from 11·358 to 11·388. Lead is soft, very tough, and makes a mark on paper; it may easily be cut with a knife or rolled into plates, but not drawn into thin wires. By repeated fusion in an open vessel, it is rendered harder and more brittle, because it becomes mixed with oxide. (Cariolis, *Ann. Chim. Phys.* 44, 103.) It has a bluish-grey colour and strong lustre. Fuses at 262° (Biot), at 282° (Newton), at 312° (Morveau), at 322° (Dalton, Crichton), at 325° (Rudberg), at 334° (Kupffer). Begins to volatilize at a very strong red heat, and boils at a white heat.

Atomic weight of Lead, 103·56. (Berzelius, *Pogg.* 19, 300.)

Compounds of Lead.

Lead and Oxygen.

A. *Suboxide of Lead?* Pb^2O.

Remains when oxalate of lead-oxide is cautiously heated in a retort from which the air is excluded. (Dulong. *Schw.* 17, 229; Boussingault, *Ann. Chim. Phys.* 79, 108; also *J. pr. Chem.* 2, 162; Pelouze, *Ann. Chim. Phys.* 79, 108; also *J. pr. Chem.* 25, 486.) The retort must be heated in the oil-bath to a temperature not exceeding 300°, the heat being continued as long as any gas is given off: the gas thus evolved is a mixture of 1 vol. carbonic oxide with 3 vol. carbonic acid, excepting towards the end of the operation, when, if the heat be somewhat increased in order to finish the decomposition, the gas evolved becomes somewhat richer in carbonic acid. (Pelouze.) The whole is suffered to cool before the suboxide is removed. It forms a black powder, sometimes dull, sometimes having a velvety lustre. (Pelouze.) It contains no metallic lead, for mercury extracts nothing from it, either dry or under water. (Boussingault, Pelouze.) Neither does it contain any yellow oxide of lead; for the aqueous solution of common sugar-of-lead does not extract any lead-oxide from it on boiling. (Pelouze.) But the suboxide, when heated to dull redness, out of contact of air, is resolved into a greenish-yellow mixture of lead and the yellow oxide. (Boussingault, Pelouze.) After this treatment, mercury extracts lead from the substance, and a boiling solution of sugar-of-lead or acetic acid leaves the lead in the form of a net-work, which, when pressed together between the fingers, forms a dense mass having the metallic lustre. (Pelouze.) When heated in the air it takes fire and burns with a glimmering light, producing 103·6 parts of yellow oxide, according to Boussingault; and from 103·6 to 103·7 according to Pelouze. Dilute sulphuric, nitric, hydrochloric, or acetic acid, resolves the suboxide into yellow oxide which combines with the acid, and very finely divided metallic lead. (Boussingault, Pelouze.) The same effect is produced by a solution of mononitrate of lead-oxide; a hot solution, on the contrary, takes up the whole of the suboxide and forms basic nitrate of lead-oxide. (Pelouze.) The suboxide, when moistened with water, rapidly absorbs oxygen from the air, and is converted into the white hydrated oxide, the action being attended with rise of temperature. (Boussingault, Pelouze.) A mixture of finely divided lead and litharge does not yield the same result. (Pelouze.) Winkelblech, by heating oxalate of lead-oxide, obtained a greyish-black powder which contained at most 1 per cent. of oxygen, and from which mercury dissolved lead; it was therefore a mixture of lead with a small quantity of

the yellow oxide. This anomalous result is attributed by Pelouze to the too great heat which Winkelblech applied to the oxalate. The grey film which forms on the surface of lead heated to a temperature short of the melting point, is likewise regarded by Berzelius as a suboxide.

Calculation, according to Boussingault and Pelouze.

2Pb	208	.....	96·29
O	8	.....	3·71
Pb^2O	216	.....	100·00

B. Lead-Oxide. PbO.

Protoxide of Lead, Yellow Oxide of Lead, Massicot, Oxide Plombique, Bleioxyd.

Formation. 1. Lead heated in the air till it volatilizes burns with a white light, and is converted into this oxide: *Flowers of Lead, Bleiblumen, Flores Plumbi.*—Lead reduced in thin metallic laminæ by the action of hydrogen gas at a gentle heat on finely crystalline lead-oxide, remains unaltered in the air at ordinary temperatures, but takes fire when heated, and burns with a feeble glow till it is converted into the protoxide. (Winkelblech.)—Lead, when heated in the air, becomes covered with a grey film, and, if the surface be continually renewed, is wholly converted into *Lead-ash* (*Bleiasche*), a yellowish-grey, pulverulent mixture of metallic lead and yellow oxide, which, if heated in the air for a longer time, is wholly converted into the latter.—2. In dry air at ordinary temperatures lead retains its lustre; in damp air, it becomes dull, assuming first a yellowish-brown, then a blue, and lastly a grey tint. (Bonsdorff, *Pogg.* 41, 305.) Under water in an open vessel, lead is converted into the hydrated oxide which partly dissolves in the water, and by absorbing carbonic acid from the air, is transformed into the hydrated carbonate. Cuttings of lead placed in a closed vessel with water and air freed from carbonic acid, and left at rest, form white flakes of hydrated lead-oxide, and the water becomes saturated with that oxide. If the vessel be shaken for half an hour, no hydrate is formed, but the lead-cuttings become covered with suboxide, and in that case, aerated water exerts no further action upon them, even if carbonic acid be likewise present. (Bonsdorff.) When lead in contact with water is exposed to the open air, white clouds of hydrated oxide consisting of soft silky scales are soon formed. (Wetzlar, *Schw.* 54, 324.) Platinum wire wound round the lead-plate accelerates the oxidation. (Fischer, *Kastn. Arch.* 17, 382.) These white scales consist of hydrated carbonate of lead-oxide; if the access of air is but partial, and consequently the process goes on slowly, the compound is obtained in silky laminæ. The finest crystals are obtained by cutting some bright places on a piece of lead tarnished by exposure to the air, and then immersing it in water; a silky vegetation then forms on the bright parts of the lead, and on removing this formation, the surface is found to be marked with crystalline devices (moiré). *Bonsdorff.*—In water containing a trace of sulphate of potash, nitre, or common salt, lead merely becomes marked with a few isolated spots; and if the water contains a larger proportion of salt, only a slight tarnishing is produced. (Wetzlar.) In saline solutions, oxidation goes on more slowly than in pure water, and the resulting product is not a loose powder, but a salt of lead closely

adhering to the surface of the metal. (Fischer.) Nitrates prevent the white turbidity only when they are in large quantity; of other salts, small quantities are sufficient: the purer, therefore, the water, the more does it become turbid by exposure to the air in contact with lead-cuttings. (Bonsdorff.)—3. Lead decomposes vapour of water at a white heat and is converted into the protoxide. (Regnault, *Ann. Chim. Phys.* 62, 363.) It does not decompose water at a red heat (Bonsdorff); neither does it decompose water acidulated with sulphuric acid at a boiling heat; but with boiling hydrochloric acid it evolves hydrogen gas.—4. With nitric acid and heated oil of vitriol it yields a lead-salt.

Preparation on the large scale.—1. *Massicot* is obtained by heating lead to low redness on a flat hearth, and continually removing the film of oxide as it forms, till the lead-ash at first obtained is, for the most part, converted into the yellow oxide; the latter is then freed from the still remaining metallic portions by grinding and levigation.—2. *Litharge* is obtained in the oxidation of *pig-lead* containing gold and silver—the resulting lead-oxide, which is generally contaminated with silica, ferric oxide, cupric and cuprous oxide, antimonic oxide, and other oxides, is fused by the high temperature, and solidifies in a scaly, shining mass, sometimes of a yellowish tint (*Argyritis, Silber-glätte*), sometimes rather inclining to red (*Chrysitis, Goldglätte*). The oxides of copper may be completely removed by digesting the levigated litharge with aqueous solution of carbonate of ammonia. (Bischof, *Schw.* 64, 65).—The antimonic oxide is left behind on dissolving the litharge in boiling nitric acid, and may then be dissolved in hydrochloric acid. (Anthon, *Repert.* 58, 387.)—¶ The difference between red and yellow litharge is attributed by Leblanc (*N. J. Pharm.* 8th Sept., 1845) to a mere diversity of physical structure, not of chemical composition; for either modification may be obtained at pleasure by properly regulating the temperature and the rate of cooling; the red variety, which is specifically lighter than the yellow and more crystalline substance, is formed most abundantly when the cooling is slow. ¶

Preparation on the small scale. By gently igniting pure crystallized nitrate, or perfectly pure carbonate or oxalate of lead-oxide, in a vessel to which the air has access.

Properties. Lead-oxide appears to be both dimorphous and amorphous. It occurs in pale yellow rhombic octohedrons (or dodecahedrons?) and cubes, and a red amorphous powder.—By the following processes, lead-oxide may be obtained in the crystalline state: 1. By slow cooling after fusion. Litharge when quickly cooled, solidifies in a mass of crystalline scales; but the portion which remains on the muffle sometimes crystallizes in yellow, translucent, six-sided tables (Marx); in rhombic octohedrons with a distinct plane of cleavage (Mitscherlich); in rhombic dodecahedrons, the angles of which are indefinite, in consequence of the curvature of the faces (Gaultier de Claubry & Beudant, *Ann. Chim. Phys.*). White lead fused by the blowpipe-flame on a copper plate or other non-reducing support, crystallizes in scales on cooling; but from the middle of it there generally shoots out a mass, half a line long, sometimes in the form of a triangular pyramid, sometimes in that of a nearly perfect rhomboidal dodecahedron, of a hyacinth-red tint while hot, becoming sulphur-yellow and translucent as it cools, and opaque and dull when perfectly cold. This alternate fusion and crystallization may be repeated

several times.—2. By fusion with hydrate of potash. If 1 part of lead-oxide and from 4 to 6 of hydrate of potash be fused for a short time in a silver crucible at an incipient red heat, and the mass after cooling exhausted with water, the lead-oxide remains in the form of cubes and square tables. (Becquerel, *Ann. Chim. Phys.* 51, 105.)—3. By treating lead-oxide with potash or soda-ley. From a solution of lead-oxide in soda-ley, saturated while hot, placed in a stoppered bottle, and then left to itself all through the winter, the lead-oxide crystallizes in small, white, translucent rhombic dodecahedrons. (Houton-Labillardière, *J. Pharm.* 3, 335.) The crystals are rhombic octohedrons, having the same angles as those obtained by fusion. (Mitscherlich.) Strong boiling potash-ley saturated with lead-oxide, yields, on cooling, yellow scales similar to those of litharge; if the potash-solution is less fully saturated with lead-oxide, or if it has deposited the excess of that oxide in scales, no further deposition takes place till after perfect cooling, whereupon red scales are thrown down, perfectly soluble in acetic acid, and therefore free from minium; if these scales are heated, they turn yellow on cooling. Hence it appears that litharge may have a red colour without containing minium or red oxide of copper. (Mitscherlich, *J. pr. Chem.* 19, 451.)—Boiling soda-ley of 40°—41° B. saturated with hydrate of lead-oxide, yields rose-red crystals of that oxide on cooling. These crystals yield an orange-yellow powder, similar to that of litharge. At about 400° they turn black, increase in bulk, decrepitate with loss of 0·1 per cent. of water—and when heated to low redness, assume a sulphur-yellow colour without changing their form. While still in the red state, they dissolve, though very sparingly, in nitric acid, either concentrated or dilute. (Calvert.)—If hydrated lead-oxide be boiled with a quantity of aqueous alkali not sufficient to dissolve it, the undissolved portion becomes converted into crystalline anhydrous oxide; the resulting solution when evaporated, yields more crystals of the anhydrous oxide, distinguished from the former portion by their easy solubility in alkalis even when dilute. (Fremy, *N. J. Pharm.* 3, 30.)—4. By precipitating a lead-salt with excess of alkali. Solution of sugar-of-lead mixed with excess of ammonia and exposed to the sun for a few days, yields olive-green, very hard crystals of anhydrous oxide. (Tünnermann, *Kastn. Arch.* 19, 339.) Behrens (*N. J. Pharm.* 4, 18) supersaturates the sugar-of-lead solution with a quantity of ammonia sufficient to re-dissolve the precipitate; filters to separate any carbonate of lead-oxide that may have been formed; puts the filtrate into a stoppered bottle; and exposes it to the rays of the sun. After a few hours, transparent crystals make their appearance, colourless at first, but afterwards becoming yellowish, and finally yellowish-grey. Their powder is white, but assumes a dark brown-red colour after long trituration.—4 measures of sugar-of-lead solution saturated at 30°, mixed with 100 measures of boiling water, and then with 45 measures of aqueous ammonia, deposit, in the course of half a minute, a large number of very delicate, yellowish-white, rhomboidal laminæ, having a silvery lustre and united in tufts; these laminæ must be separated by levigation from the crystalline granules of hydrated oxide which fall down at the same time, then washed with boiling water, and dried in vacuo. When ignited, they do not give off any water—or only a trace of it, with decrepitation—neither do they lose their transparency. They may be obtained without admixture of hydrate, by boiling 100 measures of a saturated solution of tris-acetate of lead-oxide with 50 measures of water, adding thereto a mixture of 50 measures of water at 80°, and 8 measures of aqueous

ammonia, and heating the mixture in the water-bath. In the course of a minute, crystals of the oxide separate, free from hydrate, the formation of the latter being prevented by the high temperature. (Payen, *Ann. Chim. Phys.* 66, 54; also *J. pr. Chem.* 13, 485.)—By mixing at a boiling heat the solutions of 1 At. sugar-of-lead and 1½ At. potash in a tenfold quantity of water, the oxide is obtained in delicate reddish-yellow spangles having the metallic lustre. (Winkelblech.) If solution of sugar-of-lead be dropt, with agitation, into strong lime-water heated to 88°, till crystalline scales make their appearance, and a small quantity more be then added, the scales increase rapidly in number as the liquid cools; when dry, they are yellowish-white, with a silvery lustre, and like talc to the touch; when ignited they turn red, without loss of weight, but on cooling regain their original colour, shape, and lustre. (Brendecke, *Repert.* 55, 318.)—5. By placing lead in contact with air and water. On the bottom of a leaden vessel filled with water, there are first formed a number of white flakes of hydrated dicarbonate of lead-oxide, then shining grey crystals of anhydrous oxide, partly in scales like mica, partly in rhombic dodecahedrons with cube-faces. When heated they become opaque and orange-coloured, but without losing weight or lustre. (Yorke, *Phil. Mag. J.* 5, 82.)

Lead-oxide is obtained in the amorphous state, by throwing the hydrated oxide into fused hydrate of soda and washing the residue, when cold, with water. Red mass, of the colour of minium, and yielding a reddish-yellow powder; between 300° and 400°, it assumes a brown-red colour, which it retains after cooling, but if heated above 400°, it becomes sulphur-yellow on cooling. It is distinguished from the crystallized red oxide by its very ready solubility in acids. (Calvert, *Compt. rend.* 16, 361.)

Lead-oxide, in its ordinary state, is either a lemon-yellow or a reddish-yellow powder. This may perhaps be regarded as the powder of the oxide in its yellow crystallized state. It assumes a brown-red colour whenever it is heated. Specific gravity 9·2092 (Karsten); 9·277 (Herapath); after fusion, 9·50 (Boullay). Lead-oxide fuses at a red heat, and on cooling, solidifies in a mass of crystalline scales; according to Marx, it expands in solidifying. It does not solidify to a glass on cooling, unless it contains silica. (Fuchs, *Schw.* 67,429.) A trace of silica added to fused oxide of lead, renders it vitreous. (Biewend, *J. pr. Chem.* 23, 250.) A similar effect is produced by fusion in an earthen crucible. The glass has a density of 8·01 (Le Royer & Dumas); it is transparent and yellow, or if metallic lead [or the suboxide?] be present, green. (Proust.) Lead-oxide volatilizes at a white heat, but less easily according to Fournet (*Ann. Chim. Phys.* 55, 414), than metallic lead. According to Brendecke, lead-oxide turns reddened litmus blue.

			Berthier.	Döbereiner.	Vauquelin.	J. Davy.
Pb	104	92·857	93·3	93·02	93	92·85
O	8	7·143	6·7	6.98	7	7·15
PbO	112	100·000	100·0	100·00	100	100·00

	Berzelius.	Bucholz.	Trommsdorff.	Proust.	Thomson.	Richter.
Pb	92·828	92·59	91·01	91	90·5	88·5
O	7·172	7·41	8·99	9	9·5	11·5
	100·000	100·00	100·00	100	100·0	100·0

(PbO = 1294·5 + 100 = 1394·5. Berzelius.)

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pts. litharge, a similar
lead free from arsenic.
to 300 parts, and
pts. litharge, 360 pts.
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litharge, but the sulphur is not completely oxidized when the quantity of litharge is 25 times as great as that of the antimonious sulphide. 1 part of antimonious sulphide and [illegible] litharge yield [illegible] and a dense, black, very fluid slag. With [illegible] litharge [illegible] with the same slag. With 10 litharge:—[illegible] lead with a slag which has precisely the composition of lead-scum. With [illegible] litharge:—[illegible] lead and a hyacinth-red glass. With 250 litharge:—[illegible] lead and a mass resembling litharge.—1 pt. *Sulphide of Bismuth* yields with [illegible] litharge an alloy of lead and bismuth, and a black crystalline-granular slag. With 5·12 litharge:—2·48 alloy and a dark-grey granular slag. With [illegible] litharge:—3·25 alloy, containing [illegible] per cent. [illegible] yellow mass resembling litharge.—[illegible] of *Zinc Blende* with 4·65 litharge, forms a doughy mass, and yields [illegible] parts of [illegible] (containing traces of zinc and sulphur and a [illegible] containing sulphide of lead. With [illegible] litharge:—[illegible] lead and a very fluid, black, opaque slag. With [illegible] litharge:—[illegible] lead and a dark-grey slag. With 25 litharge:—[illegible] lead and a yellow translucent glass. With this proportion of litharge, both the zinc and the sulphur are completely oxidized.—1 pt. [illegible] and [illegible] litharge, yield semi-ductile metallic lumps containing sulphide of lead, sulphide of tin, and metallic oxides. With 12 litharge:—[illegible] lead and a hyacinth-red glass. With 20 litharge:—[illegible] lead and a similar glass. With 30.. 50 litharge:—6 lead and a similar glass. Berthier. *Ann. Chim. Phys.* 39, 244.)

Combinations. *a.* With Water.—1. *Hydrate of Lead-oxide.*—Bright lead, exposed to the action of pure water and of air free from carbonic acid, forms white flakes of hydrate. (Berzelius.)—2. The hydrate may be prepared by dropping sugar-of-lead solution into excess of ammonia till the precipitate becomes permanent, then washing it and drying at a gentle heat. (Tünnermann. *Kastn. Arch.* 10, 332.) Trisacetate of lead-oxide may also be used. The precipitate must be washed out of contact of air, and dried in vacuo at 15°. (Payen. *Ann. Chim. Phys.* 66, 49; also *J. pr. Chem.* 13, 484.)—3. By mixing 4 measures of water saturated at 30° with sugar-of-lead, with 400 measures of boiling water, and then adding 4 measures of aqueous ammonia. Together with the crystals of the anhydrous oxide (pp. 110, 111), there are likewise deposited denser crystalline grains of the hydrate, which may be separated by levigation. (Payen.) To obtain larger crystals, 100 measures of water saturated at 25° with trisacetate of lead-oxide, and diluted with 60 measures of water freed from air by boiling, are mixed with 4 measures of ammonia diluted with 60 measures of water also freed from air by boiling and then cooled, and the mixture kept for some time at a temperature of 30°. The crystallization begins in an hour, and is finished in 24 hours. (Payen.)—5. By precipitating sugar-of-lead, or some other lead-salt, with potash or soda. (Mitscherlich.) Mulder (*J. pr. Chem.* 19, 79), after pouring off the liquid, boils the precipitate for some time with potash, and dries it at 100°. According to Winkelblech, potash added to nitrate or acetate of lead-oxide, even when in excess and aided by heat, does not precipitate the hydrated oxide, but a basic salt.

Hydrated lead-oxide is a white powder. When examined by the microscope, it is seen to consist (1) of transparent and colourless four-sided prisms—or, if precipitated from the trisacetate—of little stars formed by the union of four octohedrons; (2) of short, four-sided prisms with four-sided summits; (3) of regular octohedrons. (Payen.) The hydrate

Decompositions. 1. Lead-oxide is reduced to the metallic state by charcoal (very easily, and with intumescence on charcoal before the blowpipe), by carbonic oxide and by hydrogen at a low red heat. The crystalline oxide obtained by precipitating a hot sugar-of-lead solution with potash is reduced by carbonic oxide or hydrogen gas at a temperature not much above 100°. (Winkelblech.) Hydrogen gas first produces the dark grey suboxide, afterwards, at a low red heat, metallic lead. (Berzelius.) The reduction of lead-oxide at a strong red heat in crucibles (*N. Gehl.* 4, 98) is due to the action of carbonic oxide gas which penetrates the crucibles. By potassium and sodium, at temperatures somewhat below the melting points of these metals, lead-oxide is reduced, with vivid ignition, to the metallic state. By antimony, to the metallic state. By cyanide of potassium, to cyanate of potash and metallic lead (Liebig.)—2. By heating with sulphur, lead-oxide is converted into sulphurous acid and a mixture of oxide and sulphide of lead.—3. By chlorine-water, into peroxide and chloride of lead: $2PbO + Cl = PbO^2 + PbCl$. Similarly by bromine. (Löwig.)—4. Lead-oxide fused in excess with metallic sulphides, sometimes decomposes them with formation of a sulphate, as with barium; sometimes with evolution of sulphurous acid, as in the case of the heavy metals. The metal of the metallic sulphide either unites directly with the lead, or it is converted into oxide, and fuses together with a portion of the lead-oxide, while pure lead separates out; with a smaller quantity of lead-oxide, sulphide of lead is produced as well as the metal, while part of the other metallic sulphide remains undecomposed, and fuses into a slag with the metallic oxide produced and the excess of lead-oxide. (Berthier.)—1 pt. *Sulphide of Barium* and 2 to 4 pts. litharge yield without fusion a black slag, consisting of baryta and lead-oxide, which may be extracted by acetic acid, and likewise of sulphate of baryta, sulphide of lead, and metallic lead. With 30 pts. litharge, the sulphur is completely oxidized, and forms sulphate of baryta.—1 pt. *Sulphide of Manganese*, with 4 pts. litharge, evolves without fusion a large quantity of sulphurous acid, and yields a black slag, the lower part of which contains lead and sulphide of lead. With 6 pts. litharge, the mass becomes soft and doughy, and a brown slag is formed, still containing a large quantity of sulphide of manganese, with separation of 35 parts of brittle lead. With 20 parts of litharge, the mixture fuses readily, and yields a hyacinth-red glass, together with 6·2 parts of ductile lead. With 30 parts of litharge, 6·6 parts of lead separate out (consequently the sulphide of manganese is perfectly oxidized), and above it a brown-red glass.—*Tersulphide* of arsenic yields very fusible mixtures with litharge; but unless the quantity of litharge equals from 20 to 30 times that of the orpiment, only a part of the sulphur is volatilized in the form of sulphurous acid: 52 parts of orpiment and 279 of litharge yield, without separation of lead, a black mass, having the metallic lustre and a granular fracture. With 558 pts. litharge, a similar slag is formed, and below it 40 parts of ductile lead free from arsenic. With 1023 pts. litharge, the separated lead amounts to 300 parts, and the slag is dense, black, and shining. With 1302 pts. litharge, 360 pts. lead are obtained, together with a brown-black, translucent slag. With
s. litharge; 450 pts. lead and a hyacinth-red glass. With 1960
ree: 470 pts. lead, and a pale hyacinth-red glass. But it is
the quantity of lead-oxide amounts to 3120 parts, that the slag
itharge in appearance, and is perfectly free from sulphide of
ersulphide of Antimony has a strong tendency to fuse with

litharge, but the sulphur is not completely oxidized unless the quantity of litharge is 25 times as great as that of the antimonious sulphide. 1 part of antimonious sulphide and 3·8 pts. litharge yield 0·2 lead and a dense, black, very fluid slag. With 6 pts. litharge:—0·9 pts. lead with the same slag. With 10 litharge:—1·6 lead, with a slag which has precisely the composition of lead-scum. With 140 litharge:—5 lead and a hyacinth-red glass. With 250 litharge:—5·7 lead and a mass resembling litharge.—1 pt. *Sulphide of Bismuth*, yields with 2·56 pts. litharge, an alloy of lead and bismuth, and a black crystalline-granular slag. With 5·12 litharge:—2·48 alloy and a dark-grey granular slag. With 10·24 litharge:—3·25 alloy, containing 24·5 per cent. of bismuth, and a greenish-yellow mass resembling litharge.—1 pt. *Sulphide of Zinc* (*Blende*) with 4·65 litharge, forms a doughy mass, and yields 2·4 parts of brittle lead (containing traces of zinc and sulphur) and a black, metal-shining slag containing sulphide of lead. With 6·97 litharge:—2·96 brittle lead, and a very fluid, black, opaque slag. With 10 litharge:—4·3 ductile lead and a dark-grey slag. With 25 litharge:—6·5 pure lead and a yellow translucent glass. With this proportion of litharge, both the zinc and the sulphur are completely oxidated.—1 pt. *Stannic Sulphide* and 5 pts. litharge, yield semi-ductile metallic lumps, containing sulphide of lead, sulphide of tin, and metallic oxides. With 12 pts. litharge:—3·6 lead and a hyacinth-red glass. With 20 litharge:—5·4 lead and a similar glass. With 30.. 50 litharge:—6 lead and a similar glass. (Berthier, *Ann. Chim. Phys.* 39, 244.)

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turns reddened litmus-paper blue. (Berzelius, *Pogg.* 25, 396.) It retains its water and its colour at temperatures somewhat above 100°. (Mitscherlich.) According to Tünnermann, it acquires a brownish-yellow tint at a temperature below 100°. At 130° it begins to give off its water, and at 145° the whole of the water escapes, quite free from acetic acid, pure oxide being left behind. (Payen, *J. pr. Chem.* 17, 197.) It is dehydrated by boiling with strong potash-ley. (Böttger.)

			Tünnermann. (2)	Mitscherlich. (5)	Payen. (2–4)	Mulder. (5)
3PbO	336	97·39	96·07	96·5	97·35	97·31
HO	9	2·61	3·93	3·5	2·65	2·69
3PbO,HO	345	100·00	100·00	100·0	100·00	100·00

¶ Schaffner (*Ann. Pharm.* 51, 175), by precipitating acetate of lead-oxide with potash, obtained a hydrated oxide containing 96·40 lead-oxide and 3·60 water, corresponding to the formula, $2PbO + HO$. ¶

β. Aqueous Solution of Lead-oxide.—1. Clean lead in contact with water and air free from carbonic acid, yields a solution of lead-oxide which turns reddened litmus blue, gives a faint red tint to turmeric, is turned brown by sulphuretted hydrogen, and gives white precipitates with sulphuric acid and with several salts. Water freed from air by boiling does not dissolve lead when kept in contact with it in a close vessel; water which has been agitated with air becomes charged with lead-oxide in the course of two hours, the quantity dissolved amounting to between $\frac{1}{12000}$ and $\frac{1}{10000}$: it then slightly reddens turmeric, and turns reddened litmus blue; becomes turbid when shaken up in a half-filled bottle, or when boiled; yields lead at the negative and peroxide at the positive pole when acted upon by the electric current; gives a brownish-black precipitate with hydrosulphuric acid; becomes turbid immediately with carbonic acid (the turbidity, however, disappearing when the acid is in excess), or with sulphuric acid, or acid sulphate of potash or soda; more slowly with the neutral sulphates; becomes turbid when mixed with sulphate of lime or common salt, and slowly with nitre; forms with iodide of potassium a white cloud, which turns yellow on the addition of a small quantity of very dilute hydrochloric acid, together with a yellow precipitate; with chromate of potash, it forms a yellow precipitate on the addition of acetic acid. Spring-water of tolerable purity, two pounds of which contain only $1\frac{3}{4}$ grains of salts and no carbonic acid, likewise, when passed through a leaden tube 150 feet long, dissolves a quantity of lead sufficient to give a brown colour with hydrosulphuric acid. If a bright iron nail be driven through a leaden plate, and the whole immersed in water containing air, a white crystalline substance forms on the lead, and the water becomes charged with lead-oxide, while the nail does not rust at all in the immediate neighbourhood of the lead, and much less on the other parts of its surface than another nail immersed alone in the water. (Ph. Yorke, *Phil. Mag. J.* 5, 82; abstr. *Pogg.* 33, 110.) Distilled water in contact with lead and with air free from carbonic acid, dissolves $\frac{1}{10000}$ lead-oxide, acquires an alkaline reaction, and becomes turbid on exposure to the air, in consequence of the formation of hydrated dicarbonate of lead-oxide. (Bonsdorff, *Pogg.* 41, 306.) Wetzlar found that aerated water, after being placed in contact with lead, gave a very slight precipitate with hydrosulphuric acid, but no alkaline reaction. The presence of small quantities of carbonic acid, sulphuric acid, or of various salts,

prevents the solution of the lead-oxide, or greatly diminishes the quantity dissolved: this was first observed by Morveau.—1 volume of water charged with $\frac{3}{4}$ vol. carbonic acid gas dissolves a mere trace of lead-oxide in the form of carbonate, which may be detected by hydrosulphuric acid, and the lead remains quite bright; this water, after boiling, again exerts a solvent action if exposed to the air. Spring-water, 10 pounds of which contain 1·21 gr. chloride of sodium and chloride of calcium, together with 6·4 gr. carbonate of lime dissolved in excess of carbonic acid, produces a slight deposit of brownish oxide on the surface of the lead, but does not dissolve any. (Yorke.) When lead is immersed in water containing sulphate of potash, common salt, or nitre, and exposed to the air, the water takes up a mere trace of lead-oxide, recognizable by hydrosulphuric acid. (Wetzlar.) The greater the purity of spring-water, the greater is the quantity of lead which it dissolves, and the less fit are leaden pipes for conducting it. Leaden pipes should not be used for the purpose unless lead remains untarnished after 24 hours' immersion in the water; they are unfit for conducting water containing less than $\frac{1}{8000}$ of its weight of salts. If the quantity of salts exceeds this limit, and the salts consist mainly of sulphates and carbonates, leaden pipes may be used; but if they consist chiefly of chlorides, even 1 part in 4000 is not sufficient to prevent the solution of the lead. (Christison, *Phil. Mag. J.* 21, 158.)—2. Lead-oxide dissolves in water, forming the same solution. Scheele (*Opusc.* 2, 283), by placing litharge in water contained in closed vessels, and agitating occasionally for several days, obtained a solution which gave precipitates with carbonic and sulphuric acid. Lead-oxide obtained by igniting the nitrate, yields, when shaken up with water, a filtrate which has a faint, sweetish-bitter taste, turns reddened litmus blue, and is rendered turbid by carbonic acid, sulphuric acid, sulphates, common salt, and nitre; these re-agents, however, leave a portion of lead-oxide in solution, for the filtrate turns brown when treated with hydrosulphuric acid. (Wetzlar, *Schw.* 54, 324.)

The solubility of pure lead-oxide in water is denied by Tünnermann (*Kastn. Arch.* 19, 338), Brendecke (*Repert.* 53, 155, and 313), Siebold (*Repert.* 53, 174), and Herberger (*Repert.* 55, 55). The discrepancy between the results obtained by these observers and those already given, appears to arise from their having generally left the water which they placed in contact with lead, its oxide, or its hydrated oxide, freely exposed to the air, and likewise to their having sometimes strained through double or quadruple filters exposed to the air all the time. Under these circumstances, the lead-oxide dissolved in the first instance, may have been precipitated by the carbonic acid in the air.

b. With Acids, forming the Salts of Lead-oxide, or Lead-salts.—Lead-oxide has a considerable affinity for acids. Lead-salts are colourless, unless they contain a coloured acid, and of great specific gravity. Those which are soluble in water have a sweet astringent taste and redden litmus. They sustain a red heat without alteration, unless the acid is very volatile or decomposible. When heated with carbonate of soda or charcoal before the blowpipe, they yield a button of lead. Their aqueous solution is precipitated in metallic dendrites, forming the *Lead-tree, Arbor Saturni,* by zinc, cadmium, and tin, and slowly by iron. The action of zinc and cadmium is immediate and complete. Zinc, however, does not precipitate lead from an alcoholic solution of sugar-of-lead. Tin ceases to act as soon as it becomes covered with lead; if the nitrate be

the salt used, stannic oxide is afterwards precipitated together with basic nitrate of lead-oxide. Iron gives a precipitate with lead-acetate* (also with the trisacetate, Payen, *Ann. Chim. Phys.* 54, 273), but not till after some time, and on exposure to the air the lead is sometimes precipitated in large crystals; on nitrate of lead-oxide, iron acts only under the same circumstances as on stannous salts (p. 70). Manganese immersed in lead-acetate throws down a brown powder. (Fischer, *Gilb.* 72, 289; *Pogg.* 9, 262; 10, 603.) The quantity of lead-oxide in the nitrate solution must be at least equal to $\frac{1}{3000}$, in order to give a perceptible indication of reduction by zinc. (Harting.) Lead-acetate dissolved in 100...500 parts of water, mixed with hydrochloric acid and kept from contact of air, is not precipitated by copper, which only contracts a few spots even at a boiling heat; but if the air has access to the solution, the lead is precipitated in the form of a black powder. (Reinsch, *J. pr. Chem.* 24, 248.) Phosphuretted hydrogen gas slowly precipitates from lead-salts a brown phosphide of lead. (H. Rose.) Hydrosulphuric acid throws down black sulphide of lead, or if the lead-solution is very dilute, colours it brown. The limit of the brown colouring is attained, when 1 part of lead-nitrate is dissolved in 100,000 parts of water (Pfaff); when 1 part of lead (in the form of nitrate) is dissolved in 200,000 parts of water (Lassaigne); when 1 part of lead-oxide (in the form of nitrate) is dissolved in 350,000 parts of water. (Harting.) If the solution of the lead-salt contains free hydrochloric acid, the precipitate is red or yellow, and a larger quantity of hydrochloric acid prevents it altogether. A solution of 1 part of lead-acetate in 200 parts of water mixed with 5 parts of hydrochloric acid of specific gravity 1·168, gives, with hydrosulphuric acid, a brown precipitate which soon turns black; with 10 parts of hydrochloric acid, an immediate red precipitate which soon turns brown and afterwards black; with 20 parts of hydrochloric acid, a carmine-red precipitate is gradually formed, which retains its colour and consists of sulphide and chloride of lead; and with 30 to 50 parts of hydrochloric acid, a slight precipitate, but only after the addition of water. (Reinsch, *Repert.* 56, 183.) A solution of 1 part of lead-acetate in 112 parts of water, mixed with 14 parts of hydrochloric acid, gives a yellow precipitate with hydrosulphuric acid. (Reinsch, *Repert.* 56, 183.) Sulphuretted hydrogen water mixed with a large quantity of hydrochloric acid gives with lead-salts a red precipitate which soon turns black. (H. Rose.) Paper saturated with a lead-salt and then thoroughly dried, is not blackened by sulphuretted hydrogen gas. (Parnell, *J. pr. Chem.* 26, 190.) Aqueous alkaline hydrosulphates likewise throw down from lead-salts a black precipitate of lead-sulphide, insoluble in excess of the alkaline hydrosulphate. Sulphide of cadmium, and likewise the hydrated sulphides of manganese, iron, cobalt, and nickel, throw down sulphide of lead from lead-salts. (Anthon.)—Hydriodic acid or iodide of potassium added to a solution of a lead-salt, not too dilute, throws down orange-yellow iodide of lead, soluble in a large excess of iodide of potassium.—Bromide of potassium gives a white precipitate with lead-salts. (Boland.)—Hydrochloric acid and its salts precipitate chloride of lead only from somewhat concentrated solutions; the precipitate is a white crystalline powder, soluble in a large quantity of water and also in potash. A solution containing 1 part of lead-nitrate in 100 parts of water is the most dilute in which hydrochloric acid will

* By the simple term *lead-acetate*, is to be understood the *neutral* acetate, or common sugar-of-lead.

produce a precipitate. (Pfaff.)—Bromine colours lead-salts yellowish-brown, and, even when added in small quantity, throws down yellowish-brown peroxide of lead [with bromide?] on the application of heat. (Simon.) Chlorine-water added in large quantities and heated, throws down brown peroxide of lead; an aqueous mixture of chlorine and bromine produces an immediate precipitate. (Simon.) Chloride of soda produces a reddish-yellow precipitate of sesquioxide of lead, which, when heated, is converted into the brown peroxide. (Winkelblech.)—Ammonia gives with lead-salts a white precipitate, which is either the hydrated oxide or a basic salt, and is insoluble in excess of ammonia.—Potash throws down white hydrate of lead-oxide, soluble in a large excess of potash, especially when heated.—Carbonate of ammonia, potash, or soda (the bicarbonates with effervescence), throws down white carbonate of lead-oxide, insoluble in excess of the precipitant, but soluble in caustic potash. A solution of 1 part of lead (in the form of nitrate) in 50,000 parts of water is rendered slightly milky by carbonate of soda; with 100,000 parts of water a slight opalescence is produced after five minutes, and with 200,000 parts of water, after ten minutes. (Lassaigne.)—Phosphate of soda gives a white precipitate soluble in potash.—Sulphuric acid and its salts throw down white, finely pulverulent sulphate of lead-oxide. This precipitate is insoluble in cold dilute acids; it is distinguished from sulphate of baryta by the blackening which hydrosulphate of ammonia produces in it. Lead-oxide is likewise completely precipitated by sulphuric acid from a dilute solution containing excess of hydrochloric or nitric acid, provided the sulphuric acid is added in considerable quantity. (Wackenroder, *Repert.* 46, 225.) 1 part of lead-oxide (in the form of nitrate) dissolved in 20,000 parts of water is still plainly indicated by sulphuric acid added in excess (Pfaff, Harting, *J. pr. Chem.* 22, 51); 1 part of lead (in the form of nitrate) dissolved in 25,000 parts of water gives an opalescence with sulphate of soda after a quarter of an hour. (Lassaigne, *J. Chim. Med.* 8, 581.)—Chromate of potash gives with lead-salts a yellow precipitate of chromate of lead-oxide. This precipitate is insoluble in dilute nitric acid; it turns red when digested with ammonia; a basic lead-salt gives a yellowish-red precipitate. The limit of the reaction is attained with 1 part of lead-oxide in the form of nitrate, dissolved in 70,000 parts of water. (Harting.)—Arseniate of soda throws down white arseniate of lead-oxide.—Oxalic acid and alkaline oxalates give a white precipitate of oxalate of lead-oxide. The precipitation by alkaline oxalates takes place even in a solution diluted 100,000 times. (Pfaff.) Oxalic acid gives a precipitate, even in solutions containing excess of acid, provided they are dilute. (Wackenroder.)—Tincture of galls forms a straw-yellow, and ferrocyanide of potassium a white precipitate. With 1 pt. in 8000. (Pfaff.)—Bromate and chlorate of potash, and likewise ferricyanide of potassium give no precipitate with lead-salts.—Those lead-salts which are insoluble in water dissolve, for the most part, in nitric acid. The carbonate, phosphate, and sulphate are likewise soluble in a cold dilute solution of sal-ammoniac. (Brett.)

c. With certain Salifiable Bases. The compounds prepared in the dry way have sometimes a vitreous appearance. From the aqueous solutions of the compounds of lead-oxide with the alkalis, zinc throws down the lead in the metallic state. These compounds may be called *Plumbites.*

d. With Chloride of Lead.

e. With Resin, Starch, Gum, Sugar, and certain other non-acid organic substances.

B. Red Oxide of Lead. $Pb^3O^4 = 2PbO, PbO^2$.

Red Lead, Minium, Bleihyperoxydul, Deutoxyde de Plomb.—Formation.—1. By keeping the protoxide at a dull red heat for a considerable time in the air. Red lead is likewise produced—after previous formation of hydrated and aqueous lead-oxide, and hydrated dicarbonate of lead-oxide—when lead-shavings are strewn upon water, the vessel being loosely covered and then set aside for some months; the formation takes place principally on those surfaces of the lead which are exposed to the air. In a similar manner, drawings made with lead turn red in the course of twenty years. (v. Bonsdorff.)

Preparation on the large scale.—Finely pounded massicot (or litharge) is heated for 24 hours or more, either on the flat hearth of a reverberatory furnace, or in vessels lying horizontally and having wide mouths projecting from the side-openings of the furnace, the mass being frequently stirred and the heat not allowed to rise above dull redness. Litharge is too dense for the purpose and oxidizes but very imperfectly; massicot likewise, even after eight firings, each continued for 24 hours, is far from being completely converted into red lead; the softer oxide obtained by heating white lead, oxidizes much more quickly and completely. Red lead prepared from massicot by one firing of 24 hours contains 8·26 p. c. oxygen, and when ignited yields 1·17 p. c. oxygen gas; it contains 50 per cent. of real minium, and when treated with nitric acid yields 17·4 per cent. of brown peroxide of lead. After 2 firings, these quantities become respectively: 8·30; 1·22; 52·1 and 18·2;—after 3 firings: 8·43; 13·6; 58·1 and 20·3;—after 4 firings: 8·56; 1·50; 64·1 and 22·4;—after 5 firings: 8·61; 1·05; 66·2 and 23·1;—and after 8 firings: 8·79; 1·75; 74·8 and 26·0. On the other hand, minium prepared from white lead by 3 firings contains 9·24 per cent. of oxygen, gives off 2·23 per cent. of oxygen gas, contains 95·3 per cent. real minium, and when treated with nitric acid, yields 33·2 per cent. peroxide of lead. If the minium thus prepared be moderately heated in a current of oxygen gas, it afterwards evolves 2·40 per cent. of oxygen on ignition. (Dumas, *Ann. Chim. Phys.* 49, 398.)

To free commercial red lead from the yellow oxide mixed with it, Dumas digests it repeatedly with solution of lead-acetate; Berzelius and Dalton recommend treatment with cold, very dilute acetic acid; Phillips recommends 144 pts. at most, of strong acetic acid diluted with a large quantity of water to 100 of minium, inasmuch as if more acid be used, the brown peroxide is likewise formed. According to Dumas, however, peroxide of lead is always formed in the purification of minium, before the whole of the free protoxide is extracted, even when the dilutest acetic acid is employed.

Commercial red lead likewise contains all the foreign metallic oxides —such as the oxides of copper, iron and silver—with which the massicot or litharge used in preparing it is contaminated.—Red lead is likewise often adulterated with oxide of iron, red bole or brick-dust; these substances remain undissolved when the red lead is digested in warm dilute nitric acid to which a little sugar has been added; boiling hydrochloric acid extracts sesquioxide of iron from the residue. When red lead thus adulterated is ignited, there remains a mixture of yellow lead-oxide and the red substances that have been added to it.

On the small scale, red lead may be obtained by the following processes.—1. When 4 parts of lead-oxide prepared by igniting white lead are heated in a silver or platinum crucible with 1 part of chlorate of potash and 8 parts of nitre (the latter acting as a flux and thereby saving the chlorate), brown peroxide of lead is first obtained; but this, when further heated to dull redness, is converted, with intumescence and thickening of the mass, into red lead. As soon as the red lead begins to decompose at the edge of the crucible, the mass is suffered to cool, and the red lead well boiled with water containing potash.—2. By boiling peroxide of lead with aqueous plumbate of potash, or 1 part of the peroxide with 5 parts of lead-nitrate and a quantity of aqueous potash or soda sufficient to re-dissolve the hydrate of lead-oxide first precipitated, till a brown-red mixture of minium with a small quantity of the peroxide is produced, and digesting this mixture, after washing, with oxalic acid, which decomposes the peroxide without acting on the minium. [The product may contain oxalate.] The minium obtained by this process is rather dark-coloured, but it becomes brighter when rubbed up with water; it has the same composition as that which is obtained by the ordinary method. (Levol, *Ann. Chim. Phys.* 75, 108; also, *J. pr. Chem.* 22, 38.)

Scarlet, crystalline-granular powder; when heated, it first assumes a finer red colour, and then turns violet. Specific gravity 8·62 (Karsten), 8·94 (Muschenbroek), 9·082 (Herapath).

			Thomson.	Berzelius.	Dumas.	Vauquelin.
3Pb	312	90·7	88	90	90·63	91
4O	32	9·3	12	10	9·37	9
Pb^3O^4	344	100·0	100	100	100·00	100

Or:			Or:		
2PbO	224	65·12	PbO	112	32·56
PbO^2	120	34·88	Pb^2O^3	232	67·44
$2PbO,PbO^2$	344	100·00	PbO,Pb^2O^3	344	100·00

Decompositions. 1. By rather strong ignition, it is resolved into yellow lead-oxide and (2·4 p. c.: *Dumas*) of oxygen gas.—2. By many oxidizable bodies, at various temperatures, it is reduced to the yellow oxide. Aqueous sulphurous and hyponitric acid at ordinary temperatures, convert it respectively into sulphate and nitrate of lead-oxide; sulphurous acid acts very slowly in the cold, but rapidly on the application of heat. Protochloride of tin converts it, with a rise of temperature of 13°, into chloride of lead and stannic oxide. (A. Vogel, *Kastn. Arch.*, 23, 84.) It is likewise reduced by boiling with a solution of sugar.—3. With heated oil of vitriol, it yields sulphate of lead-oxide and oxygen gas.—4. With nitric acid, dilute sulphuric acid, and likewise by weaker acids, such as acetic acid, it yields peroxide of lead and a salt of the protoxide. (Berzelius.) With a small quantity of strong acetic acid, red lead forms a white mass, which dissolves in a large quantity of the acid, forming a colourless liquid, from which peroxide of lead is gradually deposited. (Berzelius.) By treating common red lead with dilute nitric acid at ordinary temperatures, Longchamp (*Ann. Chim. Phys.* 34, 105) obtained 16·66 per cent. of peroxide, and at 80°, 16·2 p. c.; from minium crystallized in fine laminæ, Houton-Labillardière, by treating it with nitric acid, obtained 25 per cent. of peroxide; Phillips (*Phil. Mag. J.* 3, 125) by

heating commercial minium with dilute nitric acid obtained 24·8 p. c. and by boiling it with moderately strong acetic acid, 25·8 p. c. of peroxide; but minium previously purified by cold dilute acetic acid yielded with nitric acid, 34 per cent. (For Dumas' results, vid. p. 119.) By heating with nitric acid, a portion of the brown oxide is decomposed and partly dissolved, forming a violet-coloured solution. (Levol.)—5. By a small quantity of hydrochloric acid, red lead is converted into chloride of lead, peroxide of lead, and water:

$$Pb^3O^4 + 2HCl = 2PbCl + PbO^2 + 2HO.$$

By a larger quantity of hydrochloric acid, into chloride of lead, chlorine gas and water:

$$Pb^3O^4 + 4HCl = 3PbCl + Cl + 4HO.$$

6. By chlorine-water, into chloride and peroxide of lead:

$$Pb^3O^4 + Cl = PbCl + 2PbO^2.$$

Similarly with bromine-water. (Löwig.)—Minium is not decomposed by mercurous nitrate or oxalic acid. (Levol.)

C. *Sesquioxide of Lead?* Pb^2O^3.

Chloride of soda throws down from lead-salts, a reddish-yellow mixture of sesquioxide and chloride of lead, which, if warmed or left to stand for some time, turns brown from formation of peroxide. To obtain the sesquioxide free from chloride, nitrate of lead-oxide is supersaturated with potash in sufficient quantity to re-dissolve the precipitate, and then treated with chloride of soda; or the precipitate obtained by treating acetate of lead-oxide with a slight excess of potash is dissolved in caustic potash (after pouring off the liquid), and the clear solution mixed with chloride of soda. The yellow precipitate, when washed and dried, yields a soft, non-crystalline, reddish-yellow powder. This powder contains more or less hygroscopic water closely united with it, and only to be got rid of by drying over vitriol with the aid of heat, whereupon it gradually escapes. At a red heat, the sesquioxide is resolved into 3·4685 per cent. of oxygen gas, and 96·5315 per cent. of protoxide. By oxalic acid and by formic acid it is reduced to the state of protoxide, with evolution of heat. With nitric, sulphuric, hydrofluosilicic and acetic acids, generally without the application of heat, it is converted into peroxide and a salt of the protoxide. It dissolves in cold hydrochloric acid, forming a yellow liquid from which it is again precipitated by alkalis: the liquid, however, resolves itself in a few minutes into chloride of lead and free chlorine. (Winkelblech.)

					Winkelblech.
2Pb	208	....	89·66	.....	89·64
3O	24	....	10·34	.....	10·36
Pb^2O^3	232	....	100·00	.....	100·00

D. Peroxide of Lead. PbO^2.

Brown Oxide of Lead, Puce Lead, Bleihyperoxyd, Tritoxyde de Plomb.—Discovered by Kurella and Scheele.—Found native in the form of *Heavy*

lead-ore (*Schwerbleierz*).—*Formation* and *Preparation*. 1. Solutions of lead-salts deposit the peroxide in crystalline scales on the positive polar wire of the voltaic circuit (I. 463). The deposition of the peroxide takes place even in a solution containing only 1 part of lead in 12,000. (Fischer, *Kastn. Arch.* 16, 219.)—2. By treating the yellow protoxide with chlorine-water (Vauquelin) or bromine-water, or aqueous hypochlorous acid.—3. Dilute subacetate of lead-oxide mixed with aqueous hypochlorous acid deposits very finely divided peroxide of lead. (Pelouze.) —4. By heating the aqueous solution of a lead-salt with chloride of soda. To a boiling solution of sugar-of-lead, chloride of soda is added as long as any precipitate is formed; the solution is then decanted, and the chloride of lead, which is precipitated at the same time, is extracted by boiling dilute nitric acid. The peroxide of lead thus obtained is somewhat lighter than that prepared by the ordinary method, but has the same composition, and contains no water. (Winkelblech.)—5. By fusing lead-oxide with chlorate of potash. (Göbel, *Schw.* 67, 77; Liebig & Wöhler, *Pogg.* 24, 172.) The preparation is made by fusing in a silver or platinum crucible, 4 parts of lead-oxide (obtained by heating white lead) with 1 part of chlorate of potash and 8 of nitre, till the mass becomes uniformly black—an effect which generally takes places simultaneously with perfect fusion—the residue is then well washed with water, and treated with dilute nitric acid. Red lead substituted for the protoxide does not yield any peroxide. (Levol, *Ann. Chim. Phys.* 75, 108.)—6. Litharge heated in a platinum crucible yields peroxide of lead and an alloy of lead and platinum. (Chevreul, *Ann. Chim. Phys.* 80, 315; also *Gilb.* 51, 115.)—7. By treating red lead with chlorine-water. Chlorine gas is passed into water in which red lead is suspended—the liquid being frequently agitated—as long as any absorption takes place; and the resulting peroxide is continually washed with boiling water to free it from chloride.—8. By treating red lead with nitric acid, which extracts the protoxide of lead. The red lead is first boiled for a sufficient time with excess of dilute nitric acid, and the resulting peroxide washed with water.—9. By fusing red lead with hydrate of potash. (Becquerel, *Ann. Chim. Phys.* 51, 104.) The potash certainly extracts protoxide of lead. Berthollet (*Stat. Chem.* 2, 377) remarked that red lead evolves no oxygen when fused with hydrate of potash.

The native peroxide occurs in six-sided prisms terminated by six-sided pyramids; specific gravity varying from 9·392 to 9·448; has an iron-black colour, with a metallic, semi-adamantine lustre, and yields a brown powder. (Breithaupt, *J. pr. Chem.*, 10, 508.) The peroxide artificially prepared by (9) appears in brown six-sided tables, exhibiting a yellow lustre by reflection; that prepared by (1) forms delicate crystalline scales, generally of a black reddish-brown colour when reduced to powder. Specific gravity of the artificial peroxide 8·903 (Herapath), 8·933 (Karsten), 9·190 (P. Boullay).

			Plattner. *Native.*	Berzelius.	Thomson.	Vauquelin.
Pb	104	86·67	86·2	86·51	80	79
2O	16	13·33	13·8	13·49	20	21
PbO^2	120	100·00	100·0	100·00	100	100

Decompositions. 1. By light into oxygen gas and red lead; in a similar manner by gentle heating; by a stronger heat it is resolved into oxygen gas and fused yellow protoxide.—2. Gives up oxygen to many

substances, sometimes with evolution of light and heat. When triturated with one-sixth of its weight of sulphur, it sets fire to the sulphur, which burns with a brilliant flame, forming sulphide of lead. (Vauquelin, *Ann. Chim. Phys.* 62, 221); a mixture of 2 parts peroxide and 1 part sulphur takes fire when touched with oil of vitriol; if the mixture likewise contains phosphorus, violent explosion takes place on trituration. (Grindel, *Schw.* 15, 478.) With aqueous hypophosphorous acid, it forms phosphate of lead-oxide. (Wartz.) When immersed in sulphurous acid gas at ordinary temperatures, it becomes red-hot, and is converted into sulphate of lead-oxide (A. Vogel, *Kastn. Arch.* 4, 434); with aqueous sulphurous acid it is likewise converted into sulphate of lead-oxide, very slowly at ordinary temperatures, more quickly with the aid of heat. Hyponitric acid dissolves it, forming a solution of nitrate of lead-oxide. With protochloride of tin it undergoes the same decomposition as red lead. (A. Vogel.) In nitrate of mercurous oxide it dissolves completely, forming nitrate of mercuric oxide and protoxide of lead. (Levol.)—When triturated with an equal weight of crystallized oxalic acid, it is decomposed without ignition, yielding vapour of water, carbonic acid gas, and carbonate of lead-oxide. It becomes incandescent when triturated with one-eighth of its weight of racemic acid, tannin, or common sugar, or with one-sixth of tartaric acid, gallic acid, grape-sugar, or manna-sugar. (Böttger.) According to A. Vogel, it is likewise converted into lead-oxide by heating with oil of turpentine or solution of sugar.—3. By heated oil of vitriol it is converted into oxygen gas and sulphate of lead-oxide.—4. By aqueous hypochlorous acid into oxygen gas (with a small quantity of chlorine) and chloride of lead. (Balard.) —5. By aqueous hydriodic, hydrobromic, hydrochloric or hydrocyanic acid, into water, iodide, bromide, chloride or cyanide of lead, and free iodine, bromine, chlorine, or cyanogen; *e. g.*

$$PbO^2 + 2HCl = PbCl + 2HO + Cl.$$

Combinations.—Peroxide of lead combines with many salifiable bases forming compounds in which it plays the part of an acid, and which may therefore be called *Salts of Plumbic Acid*, or *Plumbates.* These compounds are formed by igniting the peroxide with salifiable bases. (Vid. *Plumbate of Potash.*) In accordance with this nomenclature, red lead may be called *Plumbate of Lead-oxide.* (Fremy, *Compt. rend.* 15, 1109; also *N. J. Pharm.* 3, 30.)

Lead and Carbon.

A. *Carbide of Lead ?*—*a.* By igniting tartrate or acetate of lead-oxide in a close vessel, a carbonaceous substance is obtained which takes fire in the air and leaves protoxide of lead. (Proust.)—*b.* Cyanide of lead, or a finely divided mixture of charcoal and lead-oxide, yields on ignition a black powder, which takes fire in the air when heated, yielding globules of metallic lead. (Berzelius.)—*c.* Lead ignited with charcoal volatilizes and sublimes as a carbide in black spangles, having the metallic lustre. (John, *Berl. Jahrb.* 1820, 320.)

B. Carbonate of Lead-oxide, or Lead Carbonate.—*Carbonate of Lead.*—Litharge slowly absorbs carbonic acid from the air.—*a. Dicarbonate.*—Formed in the hydrated state by continued exposure of lead d in water to the open air. (Delaville, *N. Gehl*, 2, 682; Becquerel,

Ann. Chim. Phys. 54, 146; Yorke, *Phil. Mag. J.* 5, 82; Bonsdorff, *Pogg.* 40, 207.) If a piece of lead be left to tarnish in damp air, then scraped clean on one part, and covered with a layer of water 6 inches deep, the salt is deposited on the bright part of the metal in the form of an arborescence consisting of crystalline scales. This compound may also be formed by keeping lead-oxide for a long time under water in a vessel exposed to the air; it then swells up, and is converted into white flakes, easily separated by washing from the unaltered oxide. (Bonsdorff, *Pogg.* 40, 207.) Lead immersed in water containing $\frac{1}{300}$ pt. of potash becomes covered with a crust of carbonate. (A. Vogel.) Finely granulated lead constantly stirred about in an aqueous solution of carbonate of potash exposed to the air, forms carbonate of lead-oxide, which may be removed from time to time by levigation. (Prechtl, *J. pr. Chem.* 2, 164.) The salt thus obtained is probably pure dicarbonate, unmixed with ordinary white lead. Possibly also the so-called white lead which Gannal and Versepuy (*Compt. rend.* 16, 1327) obtained by agitating finely divided lead with water, consisted of this salt. The dicarbonate when used as a pigment has not the coating power of white lead. (Bonsdorff.) After exposure to the air for some time, it effervesces more strongly with acids than before. Water dissolves but a trace of it. (Yorke.)

				Bonsdorff.	Yorke.
2PbO	224	87·85		86·51	89·00
CO^2	22	8·62		9·93	7·66
HO	9	3·53		3·55	2·83
$2PbO,CO^2+Aq.$	255	100·00		99·99	99·49

b. Sesquibasic Carbonate.—White lead generally consists of this salt in the hydrated state. It is precipitated by carbonic acid from a solution of the acetate.—1. *New Mode of Preparation:* Carbonic acid gas passed through a solution of basic acetate of lead-oxide takes up a portion of the oxide, and is precipitated with it in the form of white lead. The gas obtained by burning charcoal in a stream of air, or that which issues from apertures on the hill-side, as at Brohl, may be used for this purpose. When carbonic acid gas is passed in five separate portions through basic lead-acetate till the liquid becomes neutral, each of the five precipitates is found to consist of $2(PbO,CO^2)+PbO,HO$. (Hochstetter.) *a. French Method:* proposed by Thénard, carried out by Roard. Distilled vinegar or a solution of sugar-of-lead is saturated with litharge—carbonic acid gas passed through it—the liquid poured off from the precipitated white lead, and again saturated with litharge—carbonic acid gas again passed through it,—and so on.—*b. English Method:* introduced by Benson. 100 parts of finely ground litharge are stirred up to the consistence of paste with the aqueous solution of 1 part of sugar-of-lead—the mixture introduced into a wooden receiver of peculiar construction—and there kept in constant agitation by means of grooved cylinders, at the same time that it is brought in contact with carbonic acid gas, generated by the combustion of coke, and cooled by passing through tubes immersed in water. When the paste, after a few days, ceases to absorb carbonic acid, it is ground with an additional quantity of water between millstones, and then levigated with water. The water dissolves out any acetate of copper or iron that may be present (*Comp.* Schabarth, *J. pr. Chem.* 24, 328.) Since lead-oxide by itself absorbs carbonic acid very slowly [and forms only the bibasic carbonate], the 100 parts of lead-oxide must

be gradually dissolved by the 1 part of sugar-of-lead and converted into basic acetate, and then precipitated from the solution by combining with carbonic acid. (Pelouze.)

2. *Older Method of Preparation.*—By exposing plates of lead to the vapours of acetic acid, and at the same time to air loaded with carbonic acid. The predisposing affinity of the acetic acid for the lead-oxide induces the formation of that compound at the expense of the air; the carbonic acid precipitates a portion of the lead-oxide from the basic acetate in the form of white lead; the acetic acid, robbed of the greater portion of its oxide, then acts upon fresh portions of lead, &c. &c. That the acetic acid, in this reaction, does not furnish the carbonic acid by any accidental decomposition, but that the latter must be introduced from some other source, and that the oxygen of the air is necessary for the oxidation of the lead, is shown by the following facts: Lead exposed to the vapours of acetic acid in air which is free from carbonic acid, yields nothing but acetate of lead. (Hochstetter.) A lead plate suspended within a vessel filled with oxygen and carbonic acid gas, and having a layer of acetic acid at bottom, produces a quantity of white lead, the oxygen and carbonic acid contained in which correspond to the quantities of those gases which disappear, but the acetic acid suffers scarcely any diminution. (Pelouze, *Ann. Chim. Phys.* 79, 112; also *J. pr. Chem.* 25, 486.) Lead moistened with acetic acid, and exposed to carbonic acid gas free from air, at a temperature between 30° and 40°, undergoes no alteration in the course of 24 hours; but if air be admitted, the metal becomes coated with white lead in the course of six hours. (Hochstetter, *J. pr. Chem.* 26, 338.) In the Dutch method of preparation, weak beer-vinegar is used containing only $1\frac{1}{2}$ per cent. of acetic acid, and a considerable quantity of acetic acid is found in the resulting white lead; hence the large quantity of carbonic acid contained in the white lead cannot be derived from the acetic acid. Formic acid in the place of acetic acid yields no white lead, because it does not form with lead-oxide a basic salt which can be decomposed by carbonic acid. (Pelouze.) *a. Dutch Method:* Earthen pots glazed inside, 8 inches high, and somewhat wider at top than at bottom, are filled to one-fourth of their depth with beer-vinegar: at one-third of their height from the bottom are three projecting points, on which a cross piece of wood is laid; on this are placed, in a vertical position, a number of leaden plates rolled up in voluminous spirals; and the whole is covered with a leaden plate. The pots are placed in rows upon horse-dung under a shed, and covered with boards, on which is laid another stratum of horse-dung; on this again is placed another row of pots,—and so on, till six rows are formed one above the other. The dung, by its slow decomposition, evolves heat, which favours the evaporation of the vinegar, and likewise gives off carbonic acid, whereby the lead-oxide is separated from the acetic acid. Circulation of air is essential to this process. In the course of 4 or 5 weeks, the greater part or the whole of the lead is converted into white lead, the change taking place from without inwards. The white lead is then detached—ground to a semi-fluid consistence while still moist—freed from adhering acetate by washing—and dried in small round pots having the form of truncated cones. Unwashed white lead still contains a large quantity of neutral acetate (Pelouze); according to Hochstetter, it contains from 2 to 12 per cent.—*b. German Method:* Plates of lead are suspended within wooden boxes placed in heated chambers, and containing

a stratum of acetic acid; or the plates are suspended in heated chambers, having their floors covered with tan and acetic acid.

When basic acetate of lead-oxide is precipitated by a very slight excess of carbonate of soda, the precipitate likewise consists of $2(PbO, CO^2) + PbO,HO$. (Hochstetter.)

White lead forms a white, earthy, dense and heavy mass, which possesses greater coating power than any other white pigment. By whichever of the preceding methods it is prepared, it is found, when diffused through water and examined by the microscope, to consist of non-crystalline, transparent, round and oval globules of the size of 0·00001, or rarely from 0·00003 to 0·00004 of an inch; the new method yields globules somewhat larger and more transparent than those obtained by the older process. (Hochstetter.)

1, *a. M* is white lead prepared in the Magdeburg factory, by the newer French method.—1, *a. Hoch.* is that prepared in the same manner on the small scale by Hochstetter.—2, *a. Holl.* is white lead from the Dutch factories, and prepared by the Dutch process.—2, *a. Hoch.* is white lead prepared by Hochstetter himself, according to the Dutch process. 2, *b. Kr.* is *Kremser white* (which contains more or less of a blue colour, probably indigo, and therefore yields a few metallic globules when ignited.) (*Mulder*).—2, *b. Off.* is white lead from Offenbach.—*Engl.* is English white lead (mode of preparation not given).—*Harz.* is white lead from a factory in the Harz (mode of preparation not given).—*Strat.* is white lead prepared in a particular manner by Stratingh, containing less hydrated oxide than the ordinary product, and consequently remaining white in the dark when mixed with poppy oil.—*Saturated.* is Dutch white lead, suspended in water and exposed for some time to a stream of carbonic acid gas.

				Hochstetter.			Mulder.	
				1, *a. M.*	1, *a. Hoch.*	2, *b. Kr.*	2, *a. Holl.*	2, *b. Kr.*
3PbO	336	86·38		85·87	86·20	86·55	86·59	86·31
$2CO^2$	44	11·31		11·77	11·45	11·27	11·71	11·35
HO	9	2·31		2·14	2·44	2·21	2·11	2·16
	389	100·00		99·78	100·09	100·03	100·41	99·82

	Link.		Hochstetter.	Mulder.		
	2, *b. Kr.*	2, *b. Off.*	*Harz.*	*Engl.*	2, *a. Holl.*	*Strat.*
PbO			86·42	86·16	85·96	86·24
CO^2	11·29	11·28	11·51	11·91	11·93	12·35
HO	2·23	2·21	2·23	1·93	1·93	1·77
			100·16	100·00	99·82	100·36

	Bette.	Malder.	Hochstetter.	
	2, *b. Kr.*	*saturated.*	2, *a. Hoch.*	2, *b. Kr.*
PbO	85·25	84·83	84·21	83·97
CO^2	12·65	15·04	14·73	15·03
HO		0·59	1·01	0·84
		100·46	99·95	99·84

Mulder (*Ann. Pharm.* 33, 242; also *J. pr. Chem.* 19, 70) dried the white lead at 130° before analyzing it, whereby it lost from 0·23 to 0·34 per cent. of hygroscopic water. Hochstetter (*J. pr. Chem.* 26, 338) and Link (*Ann. Pharm.* 46, 232), and probably also Bette (*Ann. Pharm.* 33, 251), analayzed white lead dried at 100°.—Hochstetter found in the

varieties of white lead which he examined, a small quantity of acetate of lead-oxide, which was completely extracted by boiling water, and which he regarded as the neutral acetate (sugar-of-lead). The proportion of acetic acid amounted to 0·56 per cent. in 1, *a. M*; to 0·52 in 2, *b. Kr.* upper series; to 0·34 in the Harz specimen, and to 0·70 per cent. in 2, *b. Kr.* lower series.—Mulder found in Stratingh's white lead: lead-oxide 85·74; carbonic acid 12·22; combined water 1·75; hygroscopic water 0·55; and acetic acid 0·12 (excess 0·38). In the analyses given in the preceding table, the hygroscopic water is deducted together with the acetic acid, and as much lead-oxide as the latter requires to form neutral acetate. From other kinds of white-lead, Mulder could not extract any acetic acid by boiling with milk-of-lime,—the only substance thereby extracted being a trace of chloride of calcium, proceeding from chloride of lead contained in the white lead, and probably produced by impurities in the water used in preparing it. Link, also, on distilling Kremser-white with sulphuric acid, obtained not a trace of acetic acid.—Mulder, on dissolving white lead in cold and very dilute acetic acid, found that Dutch white lead left small quantities of lead, sulphide of lead, sulphate of lead-oxide, and chloride of lead—Kremser-white and English white lead, small quantities—and Stratingh's white lead, traces of sulphate of lead-oxide and chloride of lead.—[For the analyses of Pfaff and Bischoff, vid. *Schw.* 53, 119; *J. pr. Chem.* 7, 172.]

From the analyses just given, it may be concluded that white lead is composed of $2(PbO,CO^2)+PbO,HO$, but that this compound—especially if the action of the carbonic acid be long continued—may be mixed more or less with monocarbonate, PbO,CO^2, whereby its value is increased. The smaller the quantity of hydrate that it contains, the better does it spread, and the less is it liable to turn brown;—*e. g.* that of Stratingh.—Probably, therefore, pure monocarbonate of lead-oxide, *e. g.* that prepared by precipitating a lead-salt with carbonate of potash, might be the best adapted for a pigment.

Ordinary white lead is mixed with considerable quantities of heavy spar, gypsum or chalk. Heavy spar and gypsum, likewise any sulphate of lead that may be accidentally present, are left behind when the white lead is dissolved in dilute acetic or nitric acid. When white lead containing chalk is treated with hydrochloric acid, the filtrate evaporated, and the residue digested in alcohol, a solution of chloride of calcium is obtained. Pure white lead dissolves completely in boiling dilute potash-ley; concentrated solution of potash, according to Böttger, converts it into anhydrous lead-oxide.

c. Monocarbonate.—Found native in the form of *Lead-spar* or *White lead-ore.* Sometimes it exhibits the form of the sulphide or sulphate from which it has been formed. Obtained by precipitating a normal lead-salt with an alkaline carbonate in excess. Berzelius (*Pogg.* 47, 199) precipitates nitrate of lead-oxide with carbonate of ammonia; if carbonate of soda be used as the precipitant, and the precipitate boiled with the liquid, the carbonate of lead-oxide (according to the same authority) carries down with it a small quantity of carbonate of soda. Bette precipitates sugar-of-lead with carbonate of ammonia; Mulder with carbonate of potash.—¶ According to Lefort (*N. J. Pharm.* 15, 26), the precipitate thrown down by alkaline carbonates from a hot solution of lead consists of $3PbO,2CO^2,^2HO$; the neutral carbonate PbO,CO^2 is obtained only by precipitating in the cold. ¶

The native compound belongs to the right prismatic system; Fig. 155, 56, and other forms. $u:w=62° 56'$; $u:t=122° 28'$; $\alpha:u=143° 33'$; $i:t=144° 44'$. Cleavage parallel to u. (Hauy.) Specific gravity 6·465. (Mohs.) Harder than calcspar. Colourless, transparent, with an adamantine lustre. Decrepitates when heated. The artificially prepared salt is a white powder, whose density, according to Karsten, is 6·4277.—Carbonate of lead-oxide gives off carbonic acid when ignited; dissolves very sparingly in cold water, to a greater extent in water containing sal-ammoniac, especially on the application of heat. ¶ According to Fresenius (*Ann. Pharm.* 59, 124), 1 part of the salt dissolves in 50551 parts of pure water of medium temperature; in 23450 parts of water containing a small quantity of acetate of ammonia, together with carbonate of ammonia and free ammonia; and in a somewhat smaller quantity of water containing a large quantity of nitrate of ammonia together with carbonate of ammonia and free ammonia. ¶—It combines with chloride of lead.

			Klaproth. *native.*	Bergmann. *native.*	Berzelius. *artificial.*	Bette.
PbO	112	83·58	83·67	83·51	83·46	83·49
CO^2	22	16·42	16·33	16·49	16·54	16·00
PbO,CO^2	134	100·00	100·00	100·00	100·00	99·49

	Mulder.	Chevreul.	Proust.
PbO	83·59	83·64	83·85
CO^2	16·34	16·36	16·15
	99·93	100·00	100·00

Lead-earth is earthy monocarbonate of lead-oxide.—*Zinc-lead-spar* contains 7 per cent. of zinc-carbonate united with the lead-carbonate. (Karsten, *Schw.* 65, 365.)

d. Five-fourths Carbonate?—Mononitrate or acetate of lead-oxide mixed with sesquicarbonate of soda, yields, without sensible evolution of carbonic acid, a white, heavy precipitate, which, when washed and dried in the air, resembles white lead and contains 80 per cent. of lead-oxide and 20 of carbonic acid.

e. Acid Carbonate.—Carbonate of lead-oxide is very slightly soluble in water containing carbonic acid. A solution of lead-oxide in water is rendered turbid by a small quantity of carbonic acid, but regains its transparency when treated with a larger quantity. (Wetzlar.) Lead covered with aqueous solution of carbonic acid, in a vessel containing air, begins to tarnish on the second day, and the liquid, which remains transparent, acquires a strong brown colour when treated with sulphuretted hydrogen, and yields a small white precipitate on boiling. But traces of various salts in the carbonic acid water prevent the solution of the lead. (Tünnermann.)—The solution of lead-oxide in water is rendered turbid by a small quantity of carbonic acid, but regains its clearness almost entirely under the influence of a larger quantity. The mixture reddens litmus and becomes turbid when heated or when mixed with carbonate of soda. (Wetzlar.)—White lead precipitated by carbonic acid from basic lead-acetate dissolves in carbonic acid water; the solution contains between $\frac{1}{8000}$ and $\frac{1}{5000}$ of oxide, is rendered turbid by monocarbonate and bicarbonate of potash, and coloured brown by sulphuretted hydrogen. (Yorke.) According to Fr. John (*Ann. Pharm.* 28, 117), carbonate of lead-oxide is not soluble in carbonic acid water.

Lead and Boron.

Borate of Lead-oxide, or Lead-borate.—*a. By Fusion.*—α. 112 arts of lead-oxide fused with 24 parts of boracic acid form a very soft ellow glass, which has a density of 6·4, softens even on immersion in oiling oil, is a perfect insulator, and tarnishes in hydrosulphuric acid as from formation of lead-sulphide.—β. With 48 parts of boracic acid, he glass has less colour and greater hardness.—γ. With 72 parts of oracic acid, the glass is nearly colourless and as hard as flint glass, but as a greater refracting power. (Faraday, *Pogg.* 18, 561.)

b. By Precipitation. An aqueous solution of borax added to a lead-alt throws down white flakes, which may be fused to a transparent glass; hey are slightly soluble in pure water, but insoluble in water containing a soda-salt; hence borax in excess throws down the whole of the lead rom lead-salts. (Soubeiran.) The salt precipitated by borax is $PbO,2BO^3$, nd the same proportion holds good in precipitation by quadroborate of mmonia, because, in that case, boracic acid remains in the liquid in com-ination with a very small quantity of lead-oxide. (Soubeiran, *J. Pharm.* 11, 31.) According to Tünnermann (*Kastn. Arch.* 20, 8), borax added in xcess to nitrate of lead-oxide, either at ordinary temperatures or at a oiling heat, throws down a salt containing 70·99 p. c. lead-oxide to 29·01 boracic acid. If the solution of borax is previously mixed with a uantity of boracic acid sufficient to give it a slightly acid reaction, a ulky white precipitate is thrown down containing 55·18 lead-oxide to 44·82 boracic acid.

Lead and Phosphorus.

A. Phosphide of Lead.—*a.* When phosphorus is thrown upon melted ead, or when lead-filings are ignited with an equal weight of glacial hosphoric acid, or chloride of lead with phosphorus, a compound is ormed containing not more than 15 per cent. of phosphorus: it has the olour of lead; may be cut with a knife, but splits into laminæ when ammered; tarnishes quickly when exposed to the air; and, when heated efore the blowpipe, yields a phosphorus-flame and a globule of lead. Pelletier, *Ann. Chim.* 13, 114.)—*b.* Phosphuretted hydrogen gas passed or two hours through a solution of sugar-of-lead, yields a brown preci-itate, which burns before the blowpipe with a small phosphorus-flame, orming beautifully crystallized lead-phosphate. (H. Rose, *Pogg.* 24, 26.)

B. Hypophosphite of Lead-oxide, or Lead-hypophosphite. — . Lead-oxide in excess yields with cold aqueous hypophosphorous acid a olution which exhibits an alkaline reaction, and, when neutralized with ypophosphorous acid, deposits the monobasic salt in crystalline laminæ aving a feebly acid reaction. When the acid is heated with excess of xide, lead is reduced and phosphate of lead-oxide formed. (H. Rose, *Pogg.* 12, 288).—2. By digesting recently precipitated carbonate of lead-xide with aqueous hypophosphorous acid, and then filtering and eva-orating, small, slightly rhombic prisms with dihedral summits are btained, which redden litmus and give off no water at 100°. (Wurtz, *Ann. Pharm.* 43, 227.)

	Crystallized.				Wurtz.
PbO	112·0	....	66·12	.....	66·05
PO	39·4	....	23·25	.....	23·15
2HO	18·0	....	10·63	.....	10·80
PbO,PO + 2Aq.	169·4	....	100·00	.....	100·00

When heated to redness in a retort, it gives off spontaneously inflammable phosphuretted hydrogen, and leaves phosphate of lead-oxide mixed with a very small quantity of phosphoric oxide. Dissolves with difficulty in cold water, more easily in hot water, but not in alcohol, which, on the contrary, precipitates it from the aqueous solution in pearly scales. The aqueous solution is not decomposed by boiling. Ammonia in excess throws down from it a powder containing 91·29 per cent. of lead-oxide, 1·57 acid, and 7·14 water; when the liquid filtered from this precipitate is boiled, it deposits flakes which, after drying, contain 86·83 oxide, 4·58 acid, and 8·79 water; the liquid still retains lead-oxide in solution. (H. Rose.)

The alkaline liquid obtained by saturating aqueous hypophosphorous acid with lead-oxide, if kept cold for a long time in a stoppered bottle, deposits a sandy powder, and acquires thereby the power of reddening litmus; because the salt which remains in solution is monobasic. (H. Rose.) —Wurtz did not succeed in preparing a basic salt; the alkaline hypophosphites do not precipitate basic lead-acetate; but the mixture becomes turbid even in the cold, and more quickly when heated, giving off pure hydrogen gas and depositing phosphite of lead-oxide, which is likewise the sandy powder observed by H. Rose.—A peculiar compound belonging to this head was obtained by Grotthuss. (*Phys. chem. Forschungen*, 1, 106.)

C. Phosphite of Lead-oxide, or Lead Phosphite.—*a. Quadrobasic.* —Formed by digesting recently precipitated diphosphite of lead-oxide with aqueous ammonia in a closed vessel for several weeks, and then washing with alcohol. The filtrate is free from oxide of lead. The salt when heated to redness in a retort, turns black and yields hydrogen gas free from phosphorus, and a residue which in 100 parts contains 87·03 oxide and 12·97 phosphoric acid. 100 parts of the salt evaporated with nitric acid and then heated to redness, leave 99·92 parts of lead-phosphate containing 85·80 parts of oxide. (H. Rose, *Pogg.* 9, 222.)

					H. Rose.
4PbO	448·0	....	85·92	.....	85·81
PO^3	55·4	....	10·63	.....	10·95
2HO	18·0	....	3·45	.....	3·24
4PbO,PO^3 + 2Aq.	521·4	....	100·00	.....	100·00

b. Bibasic.—To prepare this salt, terchloride of phosphorus dissolved in a large quantity of water is neutralized almost completely with ammonia; a hot aqueous solution of lead-chloride added to the liquid, the bulky precipitate freed from adhering lead-chloride by continued washing with boiling water; then pressed to remove the greater quantity of the liquid, and dried in vacuo over oil of vitriol.—White powder. (Berzelius.) Even if the washing be continued till the wash-water no longer gives a turbidity with solution of silver, the precipitate still retains a portion of lead-chloride; hence a better mode of preparation is to precipitate acetate of lead-oxide with phosphite of ammonia. (H. Rose, *Pogg.* 9, 42.)

					Berzelius.
2PbO	224·0	....	77·67	.....	77·69
PO^3	55·4	....	19·21	.....	19·16
HO	9·0	....	3·12	.....	3·15
$2PbO, PO^3 + Aq$	288·4	....	100·00	.....	100·00

The salt, when heated in a retort, turns black, gives off hydrogen gas together with a large quantity of non-spontaneously inflammable phosphuretted hydrogen, and afterwards yields pure hydrogen gas together with a tolerably large quantity of sublimed phosphorus—more than any other phosphite—and leaves a blackish residue. Since the salt prepared with chloride of lead likewise yields this blackish residue, the blackening probably arises, not from the acetic acid of the lead-acetate, but from the phosphorus; hence on dissolving in nitric acid, the black matter which separates at first is gradually dissolved. The blackish residue contains 79·01 per cent. (5 At.) lead-oxide and 20·99 per cent. (not quite 2 At.) phosphoric acid. Therefore:

$$5(2PbO, PO^3 + HO) = 10PbO, 4PO^5 + P + 5H.$$

(H. Rose, *Pogg.* 9, 221.)—The salt evolves sulphurous acid from heated oil of vitriol. (Wurtz.) When heated with nitric acid, it yields diphosphate of lead-oxide, whereas cold nitric acid dissolves it without alteration. (Berzelius, *Ann. Chem. Phys.* 2, 229.)—It dissolves very sparingly in warm phosphorous acid, and is precipitated from the solution in white flakes by ammonia. (Wurtz.)

D. Ordinary Phosphate of Lead-oxide, or Lead-phosphate.—*a. Terbasic.* 1. By digesting *b* with aqueous ammonia.—2. By precipitating neutral acetate of lead-oxide with diphosphate of soda, whereby acetic acid is set free. White; less fusible than *b*. When heated on charcoal before the blowpipe, it is reduced to *b*, while the third atom of lead-oxide is reduced. (Berzelius, Mitscherlich, Heintz.)

					Berzelius.
3PbO	336·0	....	82·47	.....	82·52
cPO^5	71·4	....	17·53	.....	17·48
$3PbO, cPO^5$	407·4	....	100·00	.....	100·00

b. Bibasic. Formed by double decomposition.—The best mode of obtaining it pure is to mix diphosphate of soda with a hot aqueous solution of chloride of lead. (Berzelius.) The alkaline diphosphate must be added drop by drop to the lead-salt, so that the latter may remain in excess: in the contrary case, a monophosphate of the alkali is formed and triphosphate of lead-oxide is precipitated. (Mitscherlich.) The salt is obtained in an impure state by mixing acetate or nitrate of lead-oxide with an aqueous solution of acid phosphate of lime, or with a solution of bone-ash in nitric acid, or with urine.—White powder, which fuses at a gentle heat, and on cooling assumes a crystalline structure, the solidification being accompanied by vivid incandescence. (Fuchs, *Schw.* 18, 292.)

	Ignited.				Berzelius.		Berthier.		Thomson.
2PbO	224·0	....	75·83	.....	76	.....	77·5	.....	80
PO^5	71·4	....	24·17	.....	24	.....	22·5	.....	20
$2PbO, PO^5$	295·4	....	100·00	.....	100	.....	100·0	.....	100

The salt melts before the blowpipe on charcoal, without reduction of the lead. (H. Rose.) When strongly ignited with charcoal, it yields lead and likewise phosphorus which volatilizes. (*Sch.* 83.) It is decomposed by sulphuric and by hydrochloric acid; dissolves in nitric acid, and in potash and soda, not in water or in acetic acid; but according to Brett, it dissolves in solution of sal-ammoniac, and is completely precipitated therefrom by a large excess of ammonia.

¶ According to Heintz (*Pogg.* 73, 122), and Gerhardt (*N. Ann. Chim. Phys.* 22, 505), the precipitate obtained by mixing solutions of chloride of lead and phosphate of soda always contains chlorine; it is in fact a double salt of phosphate and chloride of lead (*vid.* p. 150).—When nitrate of lead-oxide and ordinary phosphate of soda are mixed, a precipitate is formed consisting of two salts, one of which contains 3 At. base to 1 At. acid, and the other 2 At. base and 1 At. water to 1 At. acid. The salt containing 2 At. lead-oxide can only be obtained pure by precipitating a boiling solution of lead-nitrate with pure phosphoric acid. The precipitate is white, crystalline, and has a mother-of-pearl lustre. It fuses before the blowpipe. Its analysis agrees with the formula, $2PbO,HO,PO^5$. (Heintz.) ¶

c. 3 At. Acid to 4 At. Base.—By precipitating the hot aqueous solution of lead-chloride with excess of monophosphate of soda, and washing with hot water. White powder which reddens litmus. (Berzelius.) Probably a mixture of bibasic and monobasic salt.

	Ignited.				Berzelius.
4PbO	448·0	....	67·66	.....	69·731
$3PO^5$	214·2	....	32·34	.....	30·269
$4PbO,3PO^5$	662·2	....	100·00	.....	100·000

d. With excess of Acid.—Lead dissolves slowly in aqueous phosphoric acid, when aided by the action of the air; *a*, *b*, and *c* dissolve sparingly in that acid; the solution when evaporated yields a few horny crystals. [On the phosphates of lead-oxide, *vid. Ann. Pharm.* 68, 286; also Gerhardt, *N. Ann. Chim. Phys.* 22, 505; Heintz, *Pogg.* 73, 122.]

E. Pyrophosphate of Lead-oxide.—By precipitating a lead-salt with dipyrophosphate of soda. The precipitate dissolves in an excess of that reagent, and when boiled with ordinary diphosphate of soda, it is converted into ordinary phosphate of lead-oxide and pyrophosphate of soda. (Stromeyer.)—¶ White amorphous powder soluble in nitric acid, in caustic potash, and in pyrophosphate of soda—insoluble in ammonia, acetic acid, and sulphurous acid. (Schwarzenberg.)

					Schwarzenberg.
2PbO	224·0	....	75·83	.....	76·29
bPO^5	71·4	....	24·17	.....	23·71
$2PbO,bPO^5$	295·4	....	100·00	.....	100·00

According to Gerhardt (*N. Ann. Chim. Phys.* 23, 505), the precipitate formed by mixing an alkaline pyrophosphate with excess of lead-nitrate, consists of $2PbO,PO^5$; but, on the contrary, if the alkaline pyrophosphate is in excess, the precipitate is redissolved on the application of heat, and after it has become permanent, contains variable quantities of alkali. A definite compound, PbO,NaO,PO^5 in the form of a granular precipitate insoluble in water, may be obtained by boiling the first-mentioned precipitate with excess of pyrophosphate of soda. ¶

F. METAPHOSPHATE OF LEAD-OXIDE.—Nitrate of lead-oxide mixed with metaphosphoric acid and then with ammonia, yields a precipitate insoluble in excess of ammonia. (Persoz.)—¶ When a tolerably concentrated solution of Fleitmann & Henneberg's metaphosphate of soda, obtained by the process described in page 133, Vol. II. (see also *Ann. Pharm.* 65, 304), is mixed with an equivalent quantity of lead-nitrate, and the solution (filtered, if necessary) left to itself, crystals are obtained, which appear to belong to the oblique prismatic system. The crystals contain 1 atom of water, which they give off with intumescence when heated.

					Fleitmann & Henneberg.
PbO	111·6	....	57·92	.....	58·10
PO^5	72·0	....	37·40	.....	36·83
HO	9·0	....	4·68	.....	5·07
PbO,aPO^5,HO	192·6	....	100·00	.....	100·00

(*Ann. Pharm.* 65, 312.) ¶

LEAD AND SULPHUR.

A. ONE-FOURTH SULPHIDE OF LEAD.—A finely divided mixture of 100 parts of galena and 84 of lead heated for a quarter of an hour in a well-closed charcoal crucible placed in a wind-furnace with a strong draught, yields 144 parts of a dull, lead-coloured, fine-grained, semi-malleable, soft mixture, exhibiting a dark grey colour on the cut surface. When oxidized by nitric acid, it yields 36 per cent. of lead-sulphate, and must therefore contain 3·96 per cent. of sulphur. (Bredberg, *Pogg.* 17, 274.)

B. DISULPHIDE OF LEAD.—1. By the same process as for the preceding compound—excepting that the mixture is fused in an earthen instead of a charcoal crucible, and covered with borax—150 parts of a more brittle mixture are obtained, having a dark leaden-grey colour, a finely laminar fracture, and containing 7·207 per cent. of sulphur. (Bredberg.)—2. Sulphate of lead-oxide ignited in a charcoal crucible gives off sulphurous acid and leaves disulphide of lead, which, at a higher temperature, partly volatilizes and is partly decomposed, leaving a residue of metallic lead. (Berthier, *Ann. Chim. Phys.* 22, 240.)

C. PROTOSULPHIDE OF LEAD.—Found native in the form of *Galena*. Sulphide of lead is likewise met with, having the form of the Polymorphite from which it has been produced.—This compound is formed: 1. When sulphur is mixed with melted lead, the whole becoming red-hot. A mixture of finely divided lead and sulphur in equal numbers of atoms, placed in a glass tube and heated at one end, only so far as to induce combination, does not continue to burn unless the tube has previously been heated in boiling water. Strips of lead, which may be tolerably thick, take fire in sulphur vapour and burn with vivid glow and deposition of half-fused globules of lead-sulphide. (Winkelblech, *Ann. Pharm.* 20, 37.)—2. By heating lead-oxide with excess of sulphur.—3. By bringing hydrosulphuric acid or an alkaline hydrosulphate in contact with lead-oxide or its salts.—Becquerel (*Ann. Chim. Phys.* 53, 106), by immersing cinnabar in a solution of hydrochlorate of magnesia contained

in a glass tube, dipping a leaden plate to the bottom, and leaving the tube well closed for six weeks, obtained grey, metal-shining, regular tetrahedrons of lead-sulphide, which formed on the sides of the tube; the liquid smelt of hydrosulphuric acid and chloride of sulphur [?], and gave off sulphurous acid when treated with a stronger acid; the lower part of the lead became brittle from absorption of mercury.

The native sulphide forms crystals belonging to the regular system. *Fig.* 1, 2, 4, 6, 8, and other forms; cleavage very easy parallel to *c*. Specific gravity 7·58; harder than rock-salt; easily pulverized; of a reddish lead-grey colour; decrepitates when heated. The sulphide obtained by fusing its elements together is lead-grey, with a crystalline granular fracture; that which is precipitated by sulphuretted hydrogen, is a brown-black powder, and, according to Karsten, has a density of 7·5052 after fusion. Sulphide of lead fuses at a strong red heat, volatilizes at a stronger heat, and sublimes undecomposed, if kept from contact with the air.

Pb	104	86·66
S	16	13·34
PbS	120	100·00

	Proust.	Vauquelin.	J. Davy.	Berzelius.	Wenzel.	Döbereiner.
Pb	86	86·23	86·6	86·64	86·8	86·9
S	14	13·77	13·4	13·36	13·2	13·1
	100	100·00	100·0	100·00	100·0	100·0

Sulphide of lead when gently ignited in the air, gives off the greater part of its sulphur in the form of sulphurous acid, while metallic lead (amounting to about half the total quantity) and sulphate of lead-oxide remain behind. (Descotils, *Ann. Chim. Phys.* 55, 441.) Sulphide of lead precipitated from the nitrate by solution of sulphide of strontium, and then dried between 40° and 50°, took fire when nearly dry, and continued to burn for an hour, till it was wholly converted into sulphate. (Anthon, *Repert.* 59, 250.) Sulphide of lead dissolves in moderately strong nitric acid, giving off nitric oxide and depositing sulphur; by fuming nitric acid it is converted, with violent evolution of heat, into sulphate. Aqua-regia decomposes it with facility, forming sulphate of lead-oxide and chloride of lead.—When ignited in a current of aqueous vapour, it volatilizes, partly without decomposition; nevertheless it gives off a small quantity of hydrogen and sulphurous acid gas, and leaves sulphide of lead mixed with metallic lead and the protoxide. (Descotils.) In vapour of water it evolves hydrosulphuric acid gas, and becomes covered with a thin film of metallic lead. The first products formed are hydrosulphuric acid and lead-oxide; the latter then reacts on the remaining sulphide, yielding lead and sulphurous acid, by which, again, a large portion of the hydrosulphuric acid is decomposed. (Regnault, *Ann. Chim. Phys.* 62, 381.) Pattinson (*Schw.* 56, 201) obtained a large quantity of hydrosulphuric acid gas and a fused residue.—Sulphide of lead dissolves in strong hydrochloric acid, hydrosulphuric acid being evolved and chloride of lead produced. Chlorine gas does not decompose it at ordinary temperatures, but on the application of heat, the compound is slowly converted into chloride of sulphur and chloride of lead, the latter remaining behind. (H. Rose, *Pogg.* 42, 540.) The chloride of lead amounts to 114·68 per cent. (Fellenberg, *Pogg.* 50, 73.) When heated to whiteness in a charcoal crucible, it yields [with evolution of sulphide of carbon] first

disulphide and afterwards one-fourth sulphide of lead. (Fournet.) Hydrogen gas, at a somewhat powerful red heat, converts sulphide of lead into sulphuretted hydrogen and metallic lead. (Descotils.) H. Rose, who at Descotils' suggestion applied less heat, obtained no decomposition. 2 parts of sulphide of lead ignited in a porcelain retort with 1 part of carbonate of soda yield 53 per cent. of lead, together with an easily fusible slag, containing sulphide of lead, sulphide of sodium, and a large quantity of sulphate of lead-oxide:

$$7PbS + 4NaO = NaO, SO^3 + 3(NaS, PbS) + 4Pb.$$

The same mixture ignited in an open crucible yields 63 per cent.; and if heated in a shallow vessel, the heat being slowly raised and long continued, it yields from 75 to 80 per cent.; for the oxide which forms by contact with the air, exerts a decomposing action on the sulphide of lead which still remains dissolved in the sulphide of sodium,—and if 4 parts of dry carbonate of soda be used to 1 part of lead-sulphide, the separation of the lead is complete. The action of the air may be replaced by that of nitre. If 10 parts of galena be fused with 30 parts of carbonate of soda, and 3 parts of nitre added, the quantity of lead reduced amounts to between 75 and 78 per cent. The galena may likewise be fused with carbonate of soda and nitre at once. 1 part of sulphide of lead fused with 4 parts of black flux yields 75 parts, and with 4 parts of tartar, 80 per cent. of lead; and 1 pt. lead-sulphide ignited in a charcoal crucible with 3 or 4 parts of carbonate of soda yield from 74 to 75 per cent. of metal. Lime or baryta, heated to whiteness with sulphide of lead in a charcoal crucible, decomposes it partially, so that the slag of sulphide of lead and barium or sulphide of lead and calcium contains globules of lead mixed with it. (Berthier, *Ann. Chim. Phys.* 33, 156.) Protosulphide and protoxide of lead decompose one another without fusion. With 1 atom of sulphide and 2 atoms of litharge, the products are sulphurous acid gas and metallic lead:

$$PbS + 2PbO = 3Pb + SO^2.$$

Any excess of litharge remains undecomposed on the top of the lead; if an excess of sulphide be present, a lower sulphide is formed. But if the litharge already contains another metallic sulphide in solution, *e. g.* sulphide of zinc or sulphide of iron, it then dissolves the lead-sulphide without decomposing it. (Berthier, *Ann. Chim. Phys.* 39, 262.) According to Döbereiner (*Schw.* 17, 248), sulphide of lead may be fused with the protoxide without decomposition. Protosulphide of lead ignited with protoxide of copper, yields sulphurous acid, metallic copper, and a slag consisting of dioxide of copper and protoxide of lead. (Karsten, *Schw.* 66, 400.)—Iron separates lead from the sulphide almost entirely, even when the sulphide is dissolved in sulphide of sodium. 10 parts of sulphide of lead, 20 of dry carbonate of soda, and 2 or 3 of iron, yield from 77 to 80 per cent. of lead. (Berthier.) Recently precipitated sulphide of lead added to the aqueous solution of a copper or silver salt throws down sulphide of copper or sulphide of silver. (Anthon.) Sulphide of lead is not decomposed by aqueous sulphurous acid, nor, at a red heat, by carbonic oxide or carbonic acid gas.

D. Pentasulphide of Lead.—Lead-salts give with aqueous pentasulphide of potassium a brown-red precipitate, which, in a few seconds, is resolved into a mixture of protosulphide of lead and free sulphur. (Berzelius.)

E. HYPOSULPHITE OF LEAD-OXIDE.—Formed by precipitating nitrate of lead-oxide with hyposulphite of lime.—White powder, which blackens even below 100°. When raised to a higher temperature, out of contact of air, it gives off sulphurous acid gas, and is converted into sulphide of lead mixed with sulphate; when heated in contact with air, it burns with a feeble flame. It dissolves in 3266 parts of water. (Herschel.) Remains white at 100°, but acquires a dark colour at 200°. When heated in a retort, it yields sulphur, sulphurous acid, and 78·57 per cent. of a grey pulverulent mixture of sulphide of lead and sulphate of lead-oxide. It dissolves in aqueous alkaline hyposulphites, forming double salts. (Rammelsberg, *Pogg.* 56, 308.)

				Herschel.	Rammelsberg.
PbO	112	70		70·3	69·34
S^2O^2	48	30			
PbO, S^2O^2	160	100			

F. TETRATHIONATE OF LEAD-OXIDE.—Iodine added to aqueous hyposulphite of lead-oxide throws down iodide of lead, while tetrathionate of lead-oxide and a trace of iodide of lead remain in solution. (Fordos & Gélis.)

G. TRITHIONATE OF LEAD-OXIDE.—Aqueous trithionic acid forms with lead-salts a white precipitate which turns black when heated. (Langlois.)

H. SULPHITE OF LEAD-OXIDE, or LEAD-SULPHITE.—Formed by double decomposition. White, tasteless powder. Gives off sulphurous acid gas when heated, and leaves a mixture of sulphide and sulphate. Strong nitric acid converts it into sulphate. Sulphuric or hydrochloric acid expels sulphurous acid from it. Insoluble in water.

				Gay-Lussac.	Thomson.
PbO	112	77·77		78	74·5
SO^2	32	22·22		22	25·5
PbO, SO^2	144	100·00		100	100·0

I. HYPOSULPHATE OF LEAD-OXIDE.—*a. Tenbasic Salt.*—Formed by decomposing *b* or *c* with excess of ammonia. Soft, white powder, having an alkaline reaction, containing about 81 parts (10 At.) of lead-oxide, 5 pts. (1 At.) of acid, and 14 pts. (20 At.) of water; decomposed by carbonic acid; very sparingly soluble in water.

b. Bibasic?—By decomposing the solution of *c* with an insufficient quantity of ammonia. Very soft, white needles, having an alkaline reaction. When digested with nitric acid, this compound is converted into 85·09 per cent. of sulphate; and, if sulphuric acid be then added to the liquid, 11 per cent. more of sulphate is precipitated. It gives up its excess of lead-oxide to the carbonic acid of the air. Difficultly soluble in water.

c. Monobasic.—Carbonate of lead-oxide is dissolved at a gentle heat in aqueous hyposulphuric acid, and the solution left to spontaneous evaporation. Large crystals, permanent in the air; they belong to the hexagonal system, and are nearly identical in form with those of the hyposulphates of strontia and lime. Primary form, *Fig.* 151; $r' : r^3 = 119°$. Taste, very sweet and somewhat rough. The salt when ignited yields 69·36 per cent. of lead-sulphate. Very easily soluble in water. (Heeren.)

	Crystallized.				Heeren.
PbO	112	....	50·91	.....	51·04
S^2O^5	72	....	32·73	.....	33·01
4HO	36	....	16·36	.....	15·95
$PbO, S^2O^5 + 4Aq$	220	....	100·00	.....	100·00

K. Sulphate of Lead-oxide, or Lead-sulphate.—*a. Basic.*—1. Aqueous ammonia digested with salt, *b.* removes only a part of the sulphuric acid. (Vauquelin, *Scher. J.* 4, 56.)—2. Monosulphate of lead-oxide is rendered much more fusible by the addition of more oxide. One atom of lead-oxide forms with 1 atom of the sulphate, a colourless, easily fusible mixture, which, on cooling, crystallizes in transparent and colourless prisms; with 2 atoms of the sulphate, it fuses at commencing whiteness and yields a fibrous enamel; with 4 or 8 atoms of the sulphate, a white, translucent, somewhat crystalline glass is formed. (Berthier, *Ann. Chim. Phys.* 43, 287.)

b. Monobasic.—Found native, in the form of *Lead-vitriol.* Some specimens of the native sulphate, formed from galena, are still cleavable in the direction of the cubical faces.—This salt is formed: 1. When oil of vitriol is heated with lead.—2. Slowly, when lead is placed in contact with aqueous sulphuric acid and with the air.—3. By contact of sulphuric acid with lead-oxide or its salts.—4. By contact of sulphuric acid with red or brown peroxide of lead. Lead-oxide does not absorb the vapour of anhydrous sulphuric acid at ordinary temperatures. (H. Rose, *Pogg.* 32, 94.)—Kuhlman (*Ann. Pharm.* 38, 366) observed that when the acid vapours in a vitriol-work were made to pass from the first leaden chamber into several others, in order to condense the whole of the sulphuric acid, the leaden plates were rapidly corroded by the excess of hyponitric acid present, and sulphate of lead-oxide was formed in the shape of silky needles and laminæ, of specific gravity 6·07.

The native sulphate belongs to the right prismatic system; *Fig.* 46, 47, and other forms, produced more especially by the entry of the faces *u*, *m*, and *t*. Cleavage parallel to *i*, *y*, and *u*; $i : i' = 76° 12'$; $y : y' = 101° 32'$; $i : y = 119° 51'$ (Hauy) $u : u' = 104°$; the angles exactly equal to those of Cœlestine. (Mitscherlich.) Specific gravity 6·1691 (Karsten); 6·298 (Mohs). Hardness equal to that of calcspar. Transparent, colourless, with an adamantine lustre.—The artificial variety forms a white, loosely coherent mass, or a white powder.—Fuses at a red heat and forms a crystalline solid on cooling.

					Klaproth.		Berzelius.		Berthier.		Bucholz.
PbO	112	....	73·684	....	73·5	....	73·615	....	73·99	....	74
SO^3	40	....	26·316	....	26·5	....	26·385	....	26·01	....	26
PbO, SO^3	152	....	100·000	....	100·0	....	100·000	....	100·00	....	100

Not decomposed at the highest temperature when heated alone. When ignited with silica or clay, it gives off all its acid in the form of sulphurous acid and oxygen gas. Heated to redness with 68 per cent. of lead or 0·3 of charcoal, it yields pure vitrefied oxide; with 6 per cent. of charcoal at the same temperature, it yields 63 per cent. of metallic lead, on the surface of which a small quantity of fused oxide floats; with 9 per cent. of charcoal, sulphurous acid is evolved, and 71 per cent. of lead containing sulphur (67 lead to 4 sulphur) produced. (Berthier, *Ann. Chim. Phys.* 20, 275.) When lead-sulphate is heated to low redness with excess of charcoal, carbonic acid is evolved without any

sulphurous acid, and sulphide of lead remains behind; with equal numbers of atoms (152 lead, 6 charcoal) also, provided the temperature be kept low, nothing but carbonic acid is evolved, and only half of the salt is reduced to the state of sulphide:

$$2(PbO,SO^3) + 2C = PbO,SO^3 + PbS + 2CO^2.$$

If the heat be then raised, the sulphide and sulphate decompose each other, forming sulphurous acid and metallic lead:

$$PbO,SO^3 + PbS = 2Pb + 2SO^2$$

With 2 atoms of lead-sulphate to 1 atom of charcoal (304 lead, 6 charcoal), ½ at. sulphide of lead is produced at a moderate red heat:

$$4(PbO,SO^3) + 2C = 3(PbO,SO^3) + PbS + 2CO^2.$$

at a stronger red heat, this half-atom of sulphide, together with 1½ at. sulphate, yields sulphurous acid gas and protoxide of lead:

$$3(PbO,SO^3) + PbS = 4PbO + 4SO^2.$$

(Gay-Lussac, *Ann. Chim. Phys.* 63, 454; also *J. pr. Chem.* 11, 68.)—Sulphate of lead-oxide ignited in a current of hydrogen gas yields water, sulphurous acid, and finally hydrosulphuric acid, whilst a mixture of metallic lead and sulphide of lead is left behind. (Arfvedson, *Pogg.* 1, 73.)—When fused with an equal number of atoms of common salt, it gives off dense fumes of chloride of lead, and yields a compact grey mass with a scaly fracture. With ½ At....1 At. chloride of barium, it fuses imperfectly, giving off chloride of lead, and forming a white enamel with a granular fracture. (Berthier.)—By aqueous carbonate of ammonia or carbonate of potash, it is converted into carbonate of lead-oxide.—It dissolves completely in warm ammonia, and separates from the solution [as a basic salt?] on cooling. (Wittstein.) It is slightly decomposed by a cold solution of sal-ammoniac, to a greater extent on boiling, and completely, when repeatedly boiled with fresh quantities of sal-ammoniac, the products being chloride of lead which crystallizes on cooling, and sulphate of ammonia. (A. Vogel, *J. pr. Chem.* 2, 196.) It dissolves completely in a boiling solution of hydrochlorate or succinate of ammonia, but does not separate out on cooling. (Wittstein, *Repert.* 63, 329.) The solution in cold sal-ammoniac is precipitated by a very large excess of ammonia. (Brett.)—By solution of common salt, it is but very slightly decomposed. (Bley, *N. Tr.* 26, 2, 292.)—It dissolves in 969 parts of aqueous nitrate of ammonia of specific gravity 1·29. The solution is rendered turbid by sulphate of potash, not by sulphuric acid, because the latter sets nitric acid free, which then exerts a still stronger solvent action.—It dissolves in 47 parts of aqueous acetate of ammonia, of specific gravity 1·36, forming a solution which is precipitated by sulphuric acid and sulphate of potash. (Bischof, *Schw.* 51, 228.)—When digested with aqueous nitrate of baryta containing excess of acid, it yields nitrate of lead-oxide. (Thénard.)—It dissolves slightly in heated hydrochloric acid, the solution depositing a small quantity of chloride of lead on cooling, while free sulphuric acid remains in the liquid. (Descotils, *N. Gehl.* 2, 175.)—On evaporating the hydrochloric acid solution (but not on boiling), the chloride of lead is decomposed. (Hayes.)—Sulphate of lead oxide dissolves in nitric acid, the more readily in proportion as the acid is warmer and more concentrated. At 12·5°, it dissolves in 172 parts of

nitric acid of specific gravity 1·144. Water does not render the solution turbid, but sulphuric acid precipitates it completely; it is likewise precipitated by carbonate of ammonia. (Bischof.) Dilute nitric acid also dissolves it, though slowly; the solution is not precipitated by phosphoric or hydrochloric acid, and not at all, or but very slightly, by alkaline sulphates; it is precipitated, however, by tartaric acid, and more especially by dilute sulphuric acid: the larger the excess of nitric acid present, the greater is the quantity of sulphuric acid required to produce a precipitate. The precipitation is gradual, and if the quantity of nitric acid be not too great, almost complete. (Wackenroder, *Ann. Pharm.* 41, 319.) The solution of lead-sulphate in nitric acid yields, on evaporation, delicate needles of sulphate, and likewise octohedrons of the nitrate. (Kobell, *Kastn. Arch.* 5, 93.)—Oil of vitriol dissolves sulphate of lead-oxide more abundantly than dilute sulphuric acid; but, according to Hayes, the ordinary oil of vitriol of commerce dissolves a greater quantity than a more concentrated acid. Water separates the salt from the solution, the more completely as the dilution is carried to a greater extent, so that ultimately only a trace remains in solution. — ¶ Dupasquier (*J. pr. Chem.* 31, 417) found that sulphuretted hydrogen produced no precipitate in strong sulphuric acid which had been boiled with recently precipitated lead-sulphate; but when the acid was diluted with water, the sulphate was precipitated, and then exhibited the usual reaction with sulphuretted hydrogen; the effect produced by water is of course equally produced by any stronger base. ¶ According to Hayes (*Sill. Amer. J.* 17, 195), the cold solution of lead-sulphate in strong sulphuric acid, is also rendered turbid and precipitated by hydrochloric acid, because the chloride of lead which it forms is insoluble in cold oil of vitriol; but the precipitate disappears on heating.—In pure water, sulphate of lead-oxide is less soluble than sulphate of strontia, but more soluble than sulphate of baryta. ¶ According to Fresenius (*Ann. Pharm.* 59, 125), 1 part of lead-sulphate dissolves in 22816 parts of pure water at 11° C., and in 36504 parts of dilute sulphuric acid. ¶

L. Sulphate and Carbonate of Lead-oxide.—*a. Leadhillite.*—$(3PbO,CO^2),+PbO,SO^3$.—Yellowish or greenish white rhombic prisms, the angles of the lateral edges being equal to 107° 30′ and 72° 30′. Sp. gr.=6·3....6·5. (Brooke.)—*b. Lanarkite.*—PbO,CO^2+PbO,SO^3.—Greenish or yellowish white acute rhombohedrons and six-sided prisms, of specific gravity 6·8—7·0; effervesces slightly with nitric acid. (Brooke.)

	Leadhillite.			Stromeyer.	Thomson.
$3(PbO,CO^2)$	402	....	72·56	72·7	72·57
PbO,SO^3	152	....	27·44	27·3	27·43
	554	....	100·00	100·0	100·00

	Lanarkite.			Thomson.
PbO,CO^2	134	....	46·85	46·04
PbO,SO^3	152	....	53·15	53·96
	286	....	100·00	100·00

M. Sulphocarbonate of Lead.—According to Berzelius, lead-salts give a dark brown precipitate with sulphocarbonate of calcium, and, according to Zeise, a red precipitate with sulphocarbonate of ammonium. The deep yellow, supernatant liquid becomes colourless in the course of 24 hours. (Berzelius.) The precipitate is black after drying, takes a

polish by pressure, and when distilled, gives off bisulphide of carbon, and is converted into sulphide of lead. (Berzelius.) The precipitate is decomposed in a few hours under water at ordinary temperatures, and more slowly under alcohol, yielding sulphide of lead and bisulphide of carbon, whereby its red colour is changed to black. If it be quickly dried in vacuo over oil of vitriol, and then heated, sulphide of carbon sublimes in drops, and sulphide of lead remains behind. Cold hydrosulphate of ammonia and heated potash-ley instantly blacken the red precipitate by withdrawing the sulphide of carbon. Iodine, nitric acid, and oil of vitriol produce no change in the compound at ordinary temperatures.

Lead and Selenium.

A. Selenide of Lead.—Found as a mass closely resembling galena. Sp. gr. 6·8. (*Comp.* Zinken, H. Rose, *Pogg.* 3, 274, and 286.)—Lead and selenium combine, with evolution of light and heat, and form a grey, porous, soft mass, which becomes silver-white by burnishing. The compound when ignited in open vessels, evolves without fusion (the native selenide with decrepitation), first a small quantity of selenium, and afterwards of selenide of lead in white fumes. When roasted on charcoal before the blowpipe, it imparts a blue colour to the flame, gives off selenium, produces a red, yellow, and white deposit on the charcoal, and is gradually converted into basic selenite of lead-oxide, which immediately sinks into the charcoal, leaving a silvery film of reduced selenide of lead.—Cold nitric acid dissolves the lead, depositing red selenium, which, on the application of heat, dissolves in the form of selenious acid. (Berzelius.) The powder yields with oil of vitriol, first a brownish, then a greenish, and then a red-brown mixture. If water be added while the mixture is greenish, the colour changes to a beautiful red. (Zinken, *N. Tr.* 12, 2, 278.)—A small quantity of selenium mixed with lead, renders it whiter, less ductile, and less fusible. (Berzelius.)

					H. Rose. *Tilkerode.*		Stromeyer. *Clausthal.*
Pb	104	....	72·72	.....	71·81	.....	70·98
Se	40	....	27·28	.....	27·59	.....	28·11
Co		....		.....		.....	0·83
PbSe	144	....	100·00	.....	99·40	.....	99·92

B. Selenite of Lead-oxide, or Lead-selenite.—a. *Basic.*—By strongly igniting *b*, or by treating it with carbonate of ammonia.—Translucent, friable, fusible substance, having a crystalline fracture.

b. *Monobasic.*—Found native, sometimes alone, sometimes mixed with Tile-ore (*Kupferpecherz*).—Selenious acid and alkaline selenites precipitate lead-oxide from its solution in hydrochloric or nitric acid; in the latter case, however, the precipitate retains a small portion of nitric acid. The pure salt is obtained by precipitating aqueous chloride of lead with excess of selenite of ammonia.—White, heavy powder, which fuses almost as readily as horn-lead, forming a yellowish translucent liquid, which, on cooling, yields a white, opaque substance, having a crystalline fracture. At a strong red heat, it gives off selenious acid with ebullition, and leaves the salt *a*. Decomposed with difficulty by boiling sulphuric acid. Scarcely soluble in water, even when free selenious acid is present. (Berzelius.)—The native selenite has a globular structure, fibrous fracture, and sulphur-

yellow colour. It decrepitates when heated, without giving off water, and at a red heat fuses into black drops, evolving a small quantity of selenium, and afterwards selenious acid, when the heat is still further increased. On charcoal, before the blowpipe, it fuses to a black slag, evolving a strong odour of selenium, covering the charcoal with lead-oxide, and yielding reduced lead in ductile grains, the reduction being attended with ebullition. It dissolves in warm nitric acid without effervescence. (Karsten, *Pogg.* 46, 277.)

					Berzelius.
PbO	112		66·67		66·67
SeO^2	56		33·33		33·33
PbO, SeO^2	168		100·00		100·00

C. Seleniate of Lead-oxide, or Lead-seleniate.—By precipitating seleniate of soda with nitrate of lead-oxide (II., 240). White powder, insoluble in water. (Mitscherlich.)

Lead and Iodine.

A. Iodide of Lead.—1. Formed by precipitating a lead-salt with aqueous hydriodic acid, iodide of potassium, or iodide of iron (Gay-Lussac) or nitrate of lead-oxide by iodide of potassium (Boullay, *Ann. Chim. Phys.* 34, 46), or acetate of lead-oxide by iodide of potassium. The lead-acetate must not be in excess, otherwise oxy-iodide of lead will be precipitated together with the pure iodide. (Inglis, Brandes, *Ann. Pharm.* 10, 266.) When acetate of lead-oxide is added in successive portions to iodide of potassium, the iodide of lead is first precipitated as a yellow powder, and afterwards in yellow laminæ resembling those of mosaic gold, and the liquid, which retains a small quantity of iodide of potassium, turns acid; acetate of lead-oxide added in excess to this liquid forms pale yellow, shining scales, containing oxy-iodide of lead. If a solution of 1 part of iodide of potassium in 10 parts of water, be mixed with a very small quantity of acetic acid, the addition of lead-acetate produces crystalline iodide of lead at once; but if too much acetic acid is present, the iodide remains dissolved, and does not separate till the acid is neutralized by potash or ammonia. The crystals are finer as the solutions are more dilute. (O. Henry, *J. Pharm.* 17, 267.)—To obtain iodide of lead in fine crystals, dissolve 1 part of iodide of potassium in 10 parts of water, then add a sufficient quantity of iodine to give the liquid a slight yellowish-brown colour, and precipitate by gradually adding a dilute solution of lead-acetate. (Hoppf, *Kastn. Arch.* 22, 71.) The product may be purified by crystallization from a solution in boiling water. (Boullay, Brandes.) —When iodide of potassium is precipitated by acetate of lead-oxide mixed with acetic acid, a greenish or dark blue iodide of lead is thrown down, containing excess of iodine which cannot be extracted by water, but may be dissolved out by alchohol or by aqueous solution of potash. When iodide of iron is precipitated by acetate of lead-oxide, the precipitate contains a small quantity of iron, which may be almost wholly extracted by water acidulated with acetic acid.—2. Iodide of lead may be obtained in octohedrons by electrolytic action. (Becquerel, *vid.* I., 401.)

Orange-yellow powder, or golden-yellow, flexible six-sided laminæ (Boullay, Denot); short six-sided prisms (Inglis). Specific gravity 6·0282 (Karsten), 6·110 (P. Boullay). Acquires a reddish-yellow colour

when heated, afterwards becoming brick-red and red-brownish-black. (O. Henry, Brandes.) Fuses when somewhat strongly heated (Gay-Lussac), forming a translucent, red-brown liquid, which, on cooling, solidifies in a yellow mass. (Brandes.) Volatilizes at a strong red head. (H. Davy.)

			Brandes.	Denot.	O. Henry.	
			laminar.		*laminar.*	*pulverulent.*
Pb	104	45·22	44·98	44·10	50·27	52·00
I	126	54·78	55·02	54·85	51·15	47·38
PbI	230	100·00	100·00	98·95	101·42	99·38

O. Henry calculates his analyses differently; but his calculations are incorrect.

Iodide of lead gives off iodine when heated [in contact with the air], and the lemon-yellow mass, after cooling, dissolves for the most part in boiling water, leaving a residue of oxy-iodide of lead. (Brandes.) When heated in chlorine gas, it is converted into chloride of lead. (Brandes.)—It is decomposed by boiling with water and iron, or still more readily with zinc, yielding metallic lead, and iodide of iron or zinc, which dissolves. (Berthemot, *J. Pharm.* 13, 412.) When boiled with water and carbonate of soda, baryta, strontia, lime, or magnesia (most slowly with the last), it yields carbonate of lead-oxide, and a solution of iodide of sodium, barium, &c. (Berthemot.) Dissolves in aqueous sal-ammoniac even when cold (Brett), more abundantly in a hot solution,—and as the liquid cools, yellowish-white needles, probably of a double iodide, separate out. (Boullay.) In aqueous ammonia, or nitrate or succinate of ammonia, it slowly turns white without dissolving; in carbonate or sulphate of ammonia the change takes place more quickly. (Wittstein, *Repert.* 63, 331.)—By repeated boiling with ether, which extracts the iodine and thereby acquires an orange-yellow colour, it is converted into pale yellow oxy-iodide of lead. (A. Vogel, *J. pr. Chem.* 22, 148.)—Dissolves in 1235 parts of cold, and in 194 parts of boiling water (Denot); in 187 parts of boiling water. (Berthemot.) The solution is colourless (Denot), and if saturated while hot, deposits crystals of pure iodide of lead on cooling. (Boullay.) When this compound is dissolved in boiling water, a faint odour of iodine becomes apparent. (Caventou, *J. Pharm.* 17, 266.) The crystals of pure iodide of lead are completely soluble in water (Brandes); any oxy-iodide of lead that may be mixed with them remains undissolved. (Caventou.) The addition of acetic acid to the water does not increase the solubility of the pure iodide. (Denot, *J. Pharm.* 20, 1; also *J. pr. Chem.* 1, 425.)—Iodide of lead dissolves in a concentrated solution of iodide of potassium, sodium, barium, strontium, calcium, or magnesium, and is again completely precipitated on the addition of water. (Berthemot.)—It appears also to be slightly soluble in alcohol. (O. Henry.)

B. Oxy-iodide of Lead.—*a.* PbI,PbO.—1. By precipitating iodide of potassium with a very large excess of lead-acetate. The precipitate is left for a while in contact with the liquid, and then boiled with water to extract the free iodide of lead. The orange-yellow colour of the precipitate changes to a paler yellow, and the liquid is found to contain free acetic acid. Also when 100 parts of iodide of lead are left for several days in contact with solution of lead-acetate, and agitated every now and then, a quantity of oxy-iodide is obtained amounting to 147 or 148 parts. (Brandes, *Ann. Pharm.* 10, 269.)—Denot (*J. Pharm.* 20, 1)

drops iodide of potassium into a solution of lead-acetate which has been exposed to the air, and boils the precipitate with water.—Gregory (*J. Pharm.* 18, 24), by mixing dilute solutions of iodide of potassium and sugar of lead, obtained, on cooling, small, dingy greenish-yellow needles, mixed with a few orange-yellow crystals of iodide of lead, which could be completely removed by boiling water. The analysis of these needles is given below; Gregory regards them as diniodide of lead, Pb^2I. In subsequent trials, however, he did not succeed in obtaining these needles [probably because he did not use the lead solution in excess].—2. By precipitating iodide of potassium with ordinary subacetate of lead-oxide [which usually contains about 2 At. lead-oxide to 1 At. acetic acid]. (Brandes.)—Pale lemon-yellow precipitate, or, according to Gregory, greenish-yellow needles.—Fuses between 200° and 300°, giving off white fumes mixed with vapour of iodine, and leaves an amber-coloured, transparent, very elastic glass, containing iodine and silica, besides oxide of lead. (Denot.)—When heated in chlorine gas, it is converted into chloride of lead. (Brandes.)—When treated with acetic acid, it gives up lead-oxide, the iodide remaining undissolved. (Brandes, Denot.)—Insoluble in boiling water. Not altered by aqueous iodide of potassium. (Brandes.)

	Calculation.		
PbI	230	.....	67·25
PbO	112	.....	32·75
PbI,PbO	342	.....	100·00

Or:				Brandes.	Denot. (1)	Gregory.
2Pb	208	60·82		60·13	60·45	62·1
I	126	36·84			36·88	37·9
O	8	2·34				
	342	100·00				100·0

b. PbI,2PbO.—By precipitating trisacetate of lead-oxide with excess of iodide of potassium.—*c.* PbI,5PbO.—By decomposing sexbasic acetate of lead-oxide with excess of iodide of potassium. Denot speaks, indeed, merely of *lead-acetate* (*Acetate plombique*), but there is no doubt that he alludes to the sex-basic salt.—The compounds *b* and *c* behave like *a*, when fused. (Denot.) Oxy-iodide of lead is also formed on boiling iodide of lead with carbonate of lead-oxide in water. (Denot.)

	b.			Or:				Denot.
PbI	230	50·66		3Pb	312	68·72		67·3
2PbO	224	49·34		I	126	27·76		26·6
				2O	16	3·52		3·5
PbI,2PbO	454	100·00			454	100·00		97·4

According to Kühn (*Arch. Pharm.* [2], 50, 281), the precipitate formed by iodide of potassium in trisacetate of lead-oxide is not PbI,2PbO, but PbI,PbO + HO.—Ammonia added in excess to a boiling-hot solution of iodide of lead, forms a white precipitate, which turns yellow when gently heated, and corresponds nearly to the formula PbI,3PbO + HO.

C. Iodide of Lead and Hydrogen.—1. Aqueous hydriodic acid, exposed for some time to the air in contact with lead-filings, gradually deposits white crystals, which dissolve when the whole is boiled, and assume a finer appearance on cooling.—2. The solution of iodide of lead

in hot aqueous hydriodic acid yields the same crystals on cooling.—White crystals having a silky lustre. The compound, when kept in vacuo or in dry air, gradually gives off hydriodic acid and leaves iodide of lead: the same change takes place quickly on the application of heat. Cold water likewise extracts the hydriodic acid with only a small quantity of iodide of lead. Boiling water dissolves the salt completely, but the liquid, on cooling, deposits crystallized iodide of lead, and retains the hydriodic acid in solution. (Guyot, *J. Chim. Méd.* 12, 247.)

When fused iodide of lead is decomposed in the voltaic circuit, iodine is evolved at the positive pole, but a periodide of lead seems likewise to be formed, which evolves iodine when heated somewhat strongly. (Faraday, *Exp. Res. in El.* 1, 236; also *Pogg.* 33, 485.)

D. *Basic Periodite of Lead-oxide?*—*a. Blue Salt.*—First observed by Denot.—1. A solution of 1 At. iodine in 1 At. aqueous soda (carbonate of soda is not so good) forms with nitrate or acetate of lead-oxide, a transient violet-red precipitate, which decomposes spontaneously under water, yielding iodine and a beautiful blue powder.—2. But if only $\frac{1}{2}$ At. or $\frac{1}{3}$ At. iodine is dissolved in 1 At. soda, the blue precipitate forms immediately, and the solution retains but a trace of iodine.—3. Also, when hydrated lead-oxide is triturated with iodine precipitated by water from an alcoholic solution, a violet-red mass is obtained, which, after a while, gives off iodine and turns blue.—The blue powder gives off no iodine in vacuo; it likewise remains unaltered in water and in solutions of lead-acetate and of sugar, but the weakest acids, even the carbonic acid of the air, separate iodine from it and form a lead-salt. When heated alone, it does not evolve iodine, but turns greenish-yellow, perhaps from formation of iodide of lead and basic iodate of lead-oxide, (Durand, *N. J. Pharm.* 2, 311.)

b. Violet Salt.—Litharge exerts little or no action on a mixture of iodine and water, even with the aid of heat; but pure hydrate of lead-oxide mixed with iodine and cold water forms, in a few seconds, a pale violet-coloured compound, which, after the excess of iodine has been expelled by boiling, must be washed and then dried out of contact of air. The hydrated lead-oxide may likewise be treated with an alcoholic solution of iodine, and the excess of iodine removed by washing with alcohol.—The pale violet compound contains 83·82 per cent. (6 At.) of lead-oxide and 16·23 per cent. (1 At.) of iodine.—At a strong red heat, it gives off oxygen gas and leaves iodide of lead [mixed with oxide]. It absorbs carbonic acid from the air without evolving iodine. The stronger acids separate iodine from it. Caustic potash dissolves it gradually. It is but slowly decomposed by boiling with water, and does not yield iodine to alcohol.—To obtain the blue compound *a*, hydrated lead-oxide must be mixed with iodine and water, and a few drops of nitrate or acetate of lead-oxide added. (Jammes, *N. J. Pharm.* 3, 356.) —[Can the compound *b* be composed of $PbI + 11PbO,IO$, and the compound *a* distinguished from it by containing less oxide of lead?]

E. Iodate of Lead-oxide, or Lead-iodate.—Iodic acid and iodate of potash or soda, give an immediate precipitate with nitrate of lead-oxide. (Pleischl, *Schw.* 45, 18.)—White powder, anhydrous after drying. When gently ignited in a retort, it gives off a large quantity of iodine and oxygen gas, and leaves 52·25 per cent. of a yellowish-brown residue, containing iodide and oxide of lead, the former of which remains undis-

solved when the residue is digested in acetic acid. (Rammelsberg, *Pogg.* 44, 566.) With concentrated hydrochloric acid, it yields chlorine gas, water, dissolved terchloride of iodine, and crystalline chloride of lead. (Filhol.)

$$PbO,IO^5 + 6HCl = PbCl + ICl^3 + 6HO + 2Cl.$$

It dissolves very sparingly in water, and with some difficulty in nitric acid. (Rammelsberg.)

F. Bibasic Periodate of Lead-oxide.—Formed by precipitating nitrate of lead-oxide with bibasic periodate of soda dissolved in the smallest possible quantity of warm, dilute nitric acid. If too much nitric acid be added to the solution, the filtrate will contain periodic acid, and will then yield an additional quantity of lead-salt on digestion with carbonate of lead-oxide. Monobasic periodate of soda likewise throws down bibasic periodate of lead-oxide from a solution of the nitrate, the supernatant liquid becoming charged with free acid.—White powder, which becomes yellowish when dried or heated, or by loss of water. Decomposed by dilute sulphuric acid. Dissolves readily in dilute nitric acid, but not in aqueous periodic acid, or in pure water. (Benckiser, *Ann. Pharm.* 17, 254.)

Lead and Bromine.

A. Bromide of Lead.—1. By treating lead-oxide with aqueous hydrobromic acid. Lead-oxide treated with bromine-water is immediately converted into peroxide of lead.—2. By precipitating a lead-salt with aqueous bromide of potassium. (Balard.)—When prepared according to (2), it is a white crystalline powder. (Balard.) From a solution in hot water, it separates in white shining needles. (Löwig.) After rapid drying it has a density of 6·6302. (Karsten.) At a strong heat, it fuses into a red liquid (Balard); and if the fusion takes place in a vessel which excludes the air, the salt solidifies on cooling, in a white, horny mass. (Löwig.) When fused in contact with the air, it emits a small quantity of white fumes, and on cooling solidifies in a yellow mass consisting of oxybromide of lead. (Balard.)—Nitric acid added to pulverized bromide of lead liberates bromine, sulphuric acid causes the evolution of brominic and hydrobromic acid; the fused bromide, on the contrary, is decomposed only by boiling oil of vitriol. (Balard.) Bromide of lead dissolves sparingly in cold water, more readily in water containing hydrochloric, nitric, or acetic acid. (Löwig.) It dissolves slowly in cold aqueous hydrochlorate or nitrate of ammonia, quickly in the same solutions when warm. (Wittstein.)

					Löwig.
Pb	104·0	...	57·02	.....	59·2
Br	78·4	...	42·98	.....	40·8
PbBr	182·4	...	100·00	.....	100·0

B. Oxybromide of Lead.—1. Formed by igniting bromide of lead in the air, till it ceases to emit white fumes. (Balard.)—2. By heating bromo-carbonate of lead (p. 145) till all the carbonic acid is expelled. (Löwig.)—By placing bromide of lead for some days in contact with a solution of lead-acetate, and agitating from time to time. The filtrate contains free acetic acid. (Brandes, *Ann. Pharm.* 10, 275.)—Prepared by (1) or (2), it has a fine-yellow colour; by (3), yellowish white, but

after complete dehydration at 140°, yellowish. When heated it becomes lemon-yellow, then reddish-yellow, then brown-red, and after cooling, resumes its original yellowish-white colour. When heated to fusion, it emits dense white fumes, and, on cooling, solidifies in a yellowish-white, translucent, pearly mass. When decomposed at a high temperature by chlorine gas, it yields 94·921 per cent. of chloride of lead, and is therefore = PbBr,PbO. (Brandes.)

C. Bromate of Lead-oxide, or Lead-bromate.—1. Bromic acid and bromate of potash throw down a white powder from lead-salts, but only from concentrated solutions. (Balard.)—2. The salt may be formed by dissolving carbonate of lead-oxide in warm bromic acid, and leaving the solution to crystallize. (Rammelsberg.)—Small, shining, permanent crystals, isomorphous with those of the strontia-salt.—They do not lose their water in vacuo over oil of vitriol. At 180°, they begin to decompose, with copious evolution of gas, forming brown oxide of lead, which, at higher temperatures, is reduced to the red and then to the yellow oxide, the latter remaining in combination with bromide of lead. Soluble in 75 parts of cold water. (Rammelsberg, *Pogg.* 52, 96.)

	Crystallized.		Rammelsberg.
PbO	112·0	46·78	46·39
BrO^5	118·4	49·46	
HO	9·0	3·76	
$PbO,BrO^5 + Aq.$	239·4	100·00	

D. Bromocarbonate of Lead.—Equivalent quantities of bromide of lead and carbonate of lead-oxide, boiled with water, form an insoluble compound, which fuses readily when heated, and afterwards gives off its carbonic acid. (Löwig.)

Lead and Chlorine.

A. Chloride of Lead.—*Plumbum-corneum, Horn-lead.*—Found native as *Cotunnite.*—1. Lead absorbs chlorine gas very slowly, and without visible combustion.—2. Hydrochloric acid added to lead-oxide or its salts forms chloride of lead; and dissolved metallic chlorides added to solutions of lead-salts throw down the same compound in the form of a crystalline powder.—3. With metallic lead, hydrochloric acid forms chloride of lead, but very slowly, and only when assisted by the action of the air. The same acid boiled with metallic lead, converts it into chloride, with evolution of hydrogen gas.—When prepared by (2), it forms a white crystalline powder, known by the name of *Magisterium Plumbi;* when crystallized from a hot solution in water or aqueous acids, it forms white, silky, six-sided needles and laminæ. Fuses below a red heat, and on cooling solidifies in a white, translucent, horny mass. According to J. Davy, it does not volatilize even at a very strong red heat, provided the air be excluded. Specific gravity of the precipitated chloride 5·8022; of that which has been fused out of contact of air, 5·6824. (Karsten.)

			J. Davy.	Döbereiner.
Pb	104·0	74·6	74·22	75·76
Cl	35·4	25·4	25·78	24·24
PbCl	139·4	100·0	100·00	100·00

Or:					Berzelius.		Kirwan.
PbO	112·0	....	80·34	.....	80·26	.....	81·77
Cl—O	27·4	....	19·66	.....	19·74	.....	18·23
	139·4	....	100·00	.....	100·00	.....	100·00

When ignited in contact with the air, it partly volatilizes, together with excess of chlorine, leaving a residue of oxychloride of lead. (Döbereiner, *Schw.* 17, 255.) When fused with sulphur, it is partially converted into sulphide of lead. (A. Vogel.) It is completely decomposed by carbonic oxide, at a red heat, yielding phosgene gas and metallic lead. (Göbel, *J. pr. Pharm.* 6, 388.)—With phosphuretted hydrogen gas, at a gentle heat, it yields hydrochloric acid, phosphorus, and metallic lead. (H. Rose, *Pogg.* 24, 334.)—With aqueous hypochlorous acid, it forms peroxide of lead and chlorine gas. (Balard.)—Aqueous alkalis convert it into quadrobasic hydrochlorate of lead-oxide.—Chloride of lead dissolves slowly in 135 parts of water at 12·5° (Bischof), and in a smaller quantity of boiling water. Of cold water containing hydrochloric acid, it requires 1636 parts to dissolve it—twelve times as much, therefore, as of pure water (Bischof); hence a precipitate is formed in the aqueous solution on the addition of hydrochloric acid. (H. Rose.) On the other hand, concentrated hydrochloric acid dissolves chloride of lead abundantly, and is precipitated by water. (Gm.) A solution of chloride of calcium, even if dilute, likewise precipitates the aqueous solution of this compound, leaving a solution containing 1 part of chloride of lead in 534 parts of water. (Bischof, *Schw.* 64, 76.) The solution in strong hydrochloric acid is not precipitated by sulphuretted hydrogen; but immediately on the addition of water. (Wackenroder.) Chloride of lead dissolves somewhat abundantly in aqueous alkaline hyposulphites (Herschel), also in aqueous acetate of soda. If, therefore, 190 parts of lead-acetate dissolved in water, are mixed with 58·7 parts of common salt, from 43 to 48 parts of chloride of lead are precipitated; the filtrate, on further evaporation, gives off acetic acid, and deposits the greater part of the chloride [or oxychloride ?] of lead, so that at length only 4·4 parts remain in solution. A small quantity of common salt added to a solution of lead-acetate forms a precipitate which disappears on agitation; a small quantity of lead-acetate solution added to a solution of common salt forms a permanent precipitate; if, however, acetate of soda is mixed with the solution of common salt, no precipitate is formed. (Anthon, *Repert.* 76, 229.)—Chloride of lead dissolves very sparingly in alcohol of 76 per cent., the solubility not being increased by heat. In spirit of 94 per cent. it is insoluble. (Bischof.)

B. Oxychloride of Lead.—*a.* 3PbCl, PbO.—4 parts of chloride of lead ignited with 1 part of litharge, yield a fused, laminar, pearl-grey mixture, which, when triturated with water, swells up to a bulky mass. (Vauquelin.)

b. PbCl, PbO.—Formed by igniting chloride of lead in the air till it no longer gives off fumes, or by fusing together chloride of lead and carbonate of lead-oxide, whereby the carbonic acid is set free. The mixture while fused is of a deep-yellow colour, and as it cools, becomes first lemon-yellow, then of a pearl colour and crystalline. (Döbereiner.) If pulverized crystalline chloride of lead be left for some days in contact with a concentrated solution of lead-acetate, it takes up protoxide of lead with evolution of acetic acid, and forms a white powder, which, after washing and drying at a gentle heat, contains from 2 to 2·5 per cent. of water. At a stronger heat the water escapes, the compound assuming first a

yellowish-white and then a light yellow tint; and the residue ultimately fuses to a deep yellow liquid, which gives off white fumes, and on cooling, solidifies to a nearly white mass containing 55·36 per cent. of chloride of lead and 44·45 per cent. of oxide. (Brandes, *Ann. Pharm.* 10, 274.)

c. PbCl,2PbO.—*Mendip Lead-ore* or *Mendipite.*—Right rhombic prism. $u:u'=77°\ 33'$. Cleavage parallel to *p* and *u*. Sp. gr. = 7·077. Harder than gypsum. Yellowish-white, with an adamantine lustre; translucent. Decrepitates when heated, and appears yellower after cooling. Fuses very readily. Yields lead before the blowpipe upon charcoal, with evolution of acid vapours. The carbonate of lead-oxide, the quantity of which is variable, and the silica, are to be regarded as accidental admixtures. (Berzelius, *Pogg.* 1, 272.)—¶ This mineral is likewise found, and in a state of greater purity, at Brilow near Stadtbergen: it there occurs in connexion with calcspar and calamine. Structure crystalline. Cleavage distinct. Very slightly brittle. White, translucent, with a mother-of-pearl lustre on the cleavage-surfaces. Sp. gr. = 7·0. (Rhodius, *Ann. Pharm.* 62, 373.) ¶

	Mendipite.			Berzelius.	Rhodius.
PbCl	139·4	38·36		34·63	39·06
2PbO	224·0	61·64		55·82	60·10
PbO,CO^2				7·55	
SiO^2				1·46	
HO				0·54	
PbCl,2PbO	363·4	100·00		100·00	99·16

d. PbCl, 3PbO.—*a. Anhydrous.*—1. By fusing 1 At. chloride of lead with 3 At. of the protoxide.—2. By fusing the hydrated compound.—Greenish-yellow, with a laminar texture; yields a pale yellow powder. (Döbereiner.)—*β. Hydrated,* PbCl, 3PbO + HO, or *Quadrobasic Hydrochlorate of Lead-oxide,* 4PbO, HCl.—1. By decomposing chloride of lead with an aqueous alkali. Berzelius precipitates an aqueous solution of chloride of lead with ammonia.—2. By precipitating subacetate of lead-oxide with a solution of common salt. (Berzelius.)—3. By decomposing a solution of common salt with lead-oxide. Scheele has shown that soda may be separated from salt by this process. According to Vauquelin (*Sch. J.* 4, 51), 1 part of common salt requires 7 parts (rather more than 4 At.) of finely pounded litharge. The mixture worked up with water to a thick pulp, turns white and thickens, the lead-oxide swelling up; hence it is necessary to add repeatedly fresh quantities of water and work the mixture up again. On diluting with water after four days, and filtering, the filtrate is found to contain nothing but caustic soda with a small quantity of chloride of lead dissolved in it; but no common salt.—According to later experiments of Anthon (*Report.* 77, 105), the chloride of sodium is but half decomposed, even when ten times its weight of lead-oxide is used, and the mixture is left to stand for 12 days and frequently agitated. White flocculent mass, which when heated gives off 7 per cent. of water, and is converted into PbCl, 3PbO. Acids dissolve out the oxide of lead, and leave the chloride. The compound is almost wholly insoluble in water, slightly soluble in caustic soda. (Vauquelin.)

e. PbCl, 5PbO.—By fusing 1 atom of chloride of lead with 5 atoms of the protoxide.—Orange-yellow substance, yielding a powder of a deep yellow colour. (Döbereiner.)

f. Cassel-yellow.—Commonly prepared by fusing a mixture of 1 part of sal-ammoniac with about 10 parts of massicot, minium, or white lead.

Part of the sal-ammoniac sublimes undecomposed, so that the compound contains about 7 At. lead-oxide to 1 At. chloride. Part of the lead is at the same time reduced by the ammonia. The compound has a fine yellow colour, and crystallizes in radiated laminæ.

C. Chlorite of Lead-oxide, or Lead-chlorite.—By precipitating chlorite of baryta which contains a large quantity of free chlorous acid and is in excess, with mononitrate of lead-oxide, and washing the precipitate with water. An excess of lead-nitrate would partially dissolve the precipitate.—Sulphur-yellow, crystalline scales. Decomposes at 126° with a kind of explosion. Sets fire to flowers of sulphur which are triturated with it by means of a glass rod. Blackens at first in hydrosulphuric acid gas, then immediately turns white by conversion into sulphate of lead-oxide. With a mixture of equal parts of water and oil of vitriol, it evolves pure chlorous acid gas, especially between 40° and 50°, and yields 88·75 per cent. of lead-sulphate. (Millon, *N. Ann. Chim. Phys.* 7, 327.)

	Crystallized.				Millon.
Pb	112·0	....	65·34	.....	65·39
ClO^3	59·4	....	34·66		
PbO,ClO^3	171·4	....	100·00		

D. Chlorate of Lead-oxide.—By dissolving lead-oxide in aqueous chloric acid, the salt is obtained in white shining laminæ, the solution of which is colourless, has a rough, sweet taste, and does not redden litmus. (Vauquelin, *Ann. Chim.* 95, 127.)—¶ By cooling a hot solution of this salt, rhomboidal prisms are obtained, which become dull and opaque by exposure to the air. They are composed of PbO,ClO^5+HO. They do not deliquesce, but are easily soluble in water and in alcohol. When heated, they leave an oxychloride of lead, of yellow colour and having the constant composition: PbO, 2PbCl. (Wächter, *Ann. Pharm.* 52, 233.) ¶

E. Perchlorate of Lead-oxide.—The solution of lead-oxide in warm aqueous perchloric acid yields small prisms having a sweet but highly astringent taste, soluble in about their own weight of water, and not deliquescent. (Serullas, *Ann. Chim. Phys.* 46, 306.)

F. Chlorocarbonate of Lead.—Found native as *Horn-lead*, or *Corneous lead-ore*.—Square prisms. *Fig.* 28, 32, 33, 39, and other forms; $p:e=123°\ 6'$ (Brooke). Specific gravity=6·06. Harder than gypsum; colourless and translucent.—When 1 At. carbonate of lead-oxide is boiled with 1 At. (or more) chloride of lead and with water, the chloride is rendered insoluble by combining with the carbonate.—White, heavy powder.—Both the natural and the artificial compound fuse very easily, and at a higher temperature are converted, with ebullition and loss of 7·75 per cent. of carbonic acid, into the oxychloride of lead *b*. (Döbereiner, *Schw.* 17, 251; Berzelius, *Syst. d. Mineral.* 241.)

	Horn-lead.				Klaproth's analysis (recalculated.)
PbCl	139·4	....	50·99	.....	53·83
PbO	112·0	....	40·96	.....	42·90
CO^2	22·0	....	8·05	.....	6·00
$PbCl,PbO,CO^2$	273·4	....	100·00	.....	102·73

G. Chlorophosphite of Lead.—Lead-salts added to terchloride of phosphorus dissolved in water and neutralized with an alkali, throw down a compound of phosphite of lead-oxide and chloride of lead, from which boiling water extracts the latter. (Berzelius.)

H. Chlorophosphate of Lead.—$PbCl + 3(3PbO, cPO^5.)$—To this head belongs *Pyromorphite* (*Green Lead*-ore or *Brown Lead*-ore). Crystalline system, the hexagonal. *Fig.* 131, 135, 137, 138, and other forms. $r:r^3 = 81° 46'$; $r:\sigma = 130° 53'$. Cleavage imperfect, parallel to r and σ (if any). Sp. gr. $= 6·9 \ldots 7·0$. Hardness equal to that of apatite. Variously coloured; with a fatty lustre; translucent. Fuses easily, and, on cooling, solidifies with vivid incandescence to an angular crystalline mass. Fused with carbonate of soda upon charcoal, it yields metallic lead. Its solution in nitric acid gives a turbidity with nitrate of silver-oxide. In some of these ores, the chloride of lead is partly replaced by fluoride of calcium, and the triphosphate of lead-oxide by triphosphate of lime or trisarseniate of lead-oxide. The calcareous ores may (with Fuchs) be regarded as mixtures of Apatite and Pyromorphite. The arsenical ores fuse upon charcoal before the blowpipe and yield metallic lead. (H. Rose.)

	Pyromorphite.			Wöhler. *a.*	*b.*	*c.*	*d.*
$10PbO$	1120·0	82·26		82·29	80·55	82·46	75·59
$Cl-O$	27·4	2·01		1·98	1·99	1·95	1·89
$3cPO^5$	214·2	15·73		15·73	14·13	15·50	1·32
AsO^5					2·30	trace	21·20
Fe^2O^3				trace	trace	trace	trace
CaO							
	1361·6	100·00		100·00	98·97	99·91	100·00

Or:				Kersten. *e.*	*f.*	*g.*
$PbCl$	139·4	10·24		10·09	10·08	9 92
CaF					0·13	0·14
$3(3PbO, cPO^5)$	1222·2	89·76		89·91	89·11	89·17
$3CaO, cPO^5$					0·68	0·77
Fe^2O^3				trace		
	1361·6	100·00		100·00	100·00	100·00

	Kersten. *h.*	*i.*	*k.*
$PbCl$	9·66	10·64	10·84
CaF	0·22	0·25	1·09
$3(3PbO, cPO^5)$	89·27	81·65	77·02
$3CaO, cPO^5$	0·85	7·46	11·05
Fe^2O^3		trace	
	100·00	100·00	100·00

a. is Green Lead-ore from Tschoppau.—*b.* White variety from Tschoppau.—*c.* Ore from Leadhills, in aurora-red hexagonal prisms.—*d.* Ore from Johann Georgenstadt, in wax-yellow, acuminated prisms. (Wöhler.) —*e.* Crystallized Brown Lead-ore from Poullaouen.—*f.* The same from England.—*g.* The same from Bleistadt, of specific gravity 7·009.—*h.* The same from Mies, of specific gravity 6·983.—*i.* Botryoidal Brown Lead-ore from Mies, of specific gravity 6·444.—*k.* Botryoidal Brown Lead-ore from the Sonnenwirbel mine near Freiberg, of specific gravity 6·092.

(Breithaupt's *Polyspherite.*) (Karsten, *Schw.* 62, 1.) — In Breithaupt's *Hedyphane*, from Longbanshyttan, of specific gravity 5·496, Kersten found PbCl 10·29,—3CaO,PO^5 15·51,—3CaO,AsO^5 12·98,—3PbO,AsO^5 60·10 (loss 1·12).—In an orange-yellow phosphate of lead from Wanlockhead Vernon (*Phil. Mag. Ann.* 1, 321; also *Schw.* 52, 187) found: PbCl 10·07, 3PbO,cPO^5 87·66,--PbO,CrO^3 1·20,—lime, silica, ferric oxide, water and combustible matter, 0·40.

¶ The same compound, containing, however, an atom of water, is formed artificially on pouring a boiling solution of chloride of lead into a solution, likewise boiling, of phosphate of soda, the latter being in excess. The precipitate is insoluble in water, but dissolves in nitric acid, which converts it into the phospho-nitrate of lead-oxide discovered by Berzelius (p. 158). The composition of the precipitate is: 3(3PbO,PO^5) + PbCl + HO. (Heintz, *Pogg.* 73, 122.)—When, on the contrary, a boiling solution of phosphate of soda is poured into an excess of chloride of lead, a precipitate is formed, which, according to Heintz, is composed of 2(3PbO,PO^5) + PbCl), but, according to Gerhardt (*N. Ann. Chim. Phys.* 22, 505), of 2PbO,HO,PO^5 + PbCl. The same compound may be formed when a phosphate is precipitated by a lead-solution in presence of a soluble chloride. ¶

I. Chlorosulphide of Lead.—When a lead-salt, *e.g.* aqueous chloride of lead, is precipitated by a mixture of sulphuretted hydrogen water and hydrochloric acid, there is produced, first a yellowish-red and then a red precipitate containing about 56 per cent. (3 At.) of sulphide and 44 per cent. (2 At.) of chloride of lead. An excess of sulphuretted hydrogen water turns it black and converts it into pure sulphide of lead; the same change is produced by boiling with water, which extracts the chloride; the compound is also blackened by potash, which extracts the chlorine. (Hünefeld, *J. pr. Chem.* 7, 27.)—When sulphuretted hydrogen is passed through a solution of ½ pt. lead-acetate in 100 parts of water mixed with 10 parts of hydrochloric acid of specific gravity 1·168, a beautiful carmine-coloured precipitate of chlorosulphide of lead is produced. If the solution contains 1 part of lead-acetate, 112 parts of water, and 14 of strong hydrochloric acid, sulphuretted hydrogen produces a yellow precipitate, which gives up chloride of lead to boiling water, while black protosulphide of lead remains behind.—If, instead of 14 parts of strong hydrochloric acid, we use 14 parts of a mixture of 2 parts of strong hydrochloric and 1 pt. nitric acid, prepared two days before and containing hyponitric acid, the sulphuretted hydrogen produces, after a while, first a yellowish-red and then a cinnabar-red, granular precipitate. (If the stream of sulphuretted hydrogen were continued for a longer time, the precipitate would become first carmine-coloured, then brown, and lastly black.) The granular precipitate, when boiled with water, gives up a considerable quantity of chloride of lead, and is converted into a brown-red, flocculent powder, which then undergoes no further change, but when heated alone in a glass tube, gives off sulphur and hydrosulphuric acid, and fuses to a brown mass. According to this reaction, the hyponitic acid must have precipitated sulphur from the hydrosulphuric acid, and the red precipitate is a compound of chloride with polysulphide of lead. (Reinsch, *Repert.* 56, 183; *J. pr. Chem.* 13, 130.)

K. Chlorosulphate of Lead. — 1 At. chloride of lead fuses readily with 1, 2, or 4 At. sulphate of lead-oxide, forming a thin liquid. With

1 At. lead-sulphate, a white, crystalline, slightly blistered enamel is obtained; with 2 or 4 At. the enamel is slightly crystalline. (Berthier, *Ann. Chim. Phys.* 43, 298.)

L. Chloriodide of Lead.—Cold hydrochloric acid has no sensible action on iodide of lead; the same acid, when boiling, dissolves the iodide, forming a pale reddish-yellow solution, and on cooling yields pale yellow four-sided needles, from which water gradually extracts the chloride of lead. (Labouré, *N. J. Pharm.* 4, 328.)

Lead and Fluorine.

A. Fluoride of Lead.—Lead is not attacked by hydrofluoric acid at any temperature below the boiling point of that acid. (Gay-Lussac & Thénard.)—The fluoride is formed by precipitating the subacetate or normal acetate of lead-oxide with hydrofluoric acid (Scheele, Gay-Lussac & Thénard), or by treating carbonate of lead-oxide with hydrofluoric acid (Berzelius), or with an alkaline hydrofluate. (Scheele.)—White, non-crystalline powder (Scheele), which fuses readily and then solidifies in a yellow mass. (Berzelius.)—Not decomposed by heating in closed vessels, but evolves hydrofluoric acid when heated in contact with air or vapour of water. (Berzelius.)—When heated with sulphur in a glass retort, it yields sulphide of lead, sulphurous acid gas, and gaseous fluoride of silicium. Phosphorus and iodine scarcely act upon it. (Unverdarben, *N. Tr.* 9, 1, 33.)—Oil of vitriol separates hydrofluoric acid from it, even at ordinary temperatures. (Gay-Lussac & Thénard.) Aqueous ammonia withdraws from it a quantity of acid just sufficient to convert it into the following compound. Fluoride of lead is very sparingly soluble in water and not more abundantly in aqueous hydrofluoric acid (Berzelius, *Pogg.* 1, 31); it dissolves more abundantly in hydrochloric and in nitric acid (Gay-Lussac & Thénard), and is decomposed on the evaporation of the dissolving acid. (Berzelius.)

B. Oxyfluoride of Lead.—1. Formed by decomposing fluoride of lead with aqueous ammonia.—2. By fusing the fluoride of an alkali-metal with lead-oxide, and washing the pulverized mass with water; the oxyfluoride is then left undissolved.—Has an astringent taste. Dissolves in pure water after removal of the saline liquid. The solution, when exposed to the air, deposits a crust consisting of carbonate of lead-oxide and fluoride of lead. (Berzelius.)

C. Borofluoride of Lead.—PbF,BF^3.—Formed by adding carbonate of lead-oxide in small portions to tetra-hydrofluate of boracic acid, till a precipitate is formed. The solution, evaporated to a syrup and then cooled, deposits long needles; but by slow evaporation, four-sided prisms or tables are obtained. Taste, sweet and astringent, afterwards somewhat sour. By continued boiling with water or alcohol, it is resolved into an *acid* salt which dissolves, and a *basic* salt which remains behind and forms a white powder. Another easily fusible basic compound is obtained by heating the borofluoride of lead with lead-oxide. (Berzelius.)

D. Chlorofluoride of Lead.—$PbCl,PbF$.—1. By precipitating aqueous fluoride of sodium with a boiling aqueous solution of chloride of lead.—2. By precipitating an aqueous solution of 2 parts of fluoride of sodium and 3 parts of common salt with sugar-of-lead.—White powder

which fuses when heated, without giving off water or acid. Slightly soluble in water, and without alteration of the proportion of the constituents in the residue. Easily soluble in nitric acid. (Berzelius.)

LEAD AND NITROGEN.

A. NITRITE OF LEAD-OXIDE, or LEAD-NITRITE.—*a. Quadrobasic.*—Formed by boiling 1 part of mononitrate of lead-oxide and 1½ parts or more of metallic lead in a long-necked flask for 12 hours, then filtering and leaving the salt to crystallize by cooling. (Berzelius, *Gilb.* 40, 194 and 200; 46, 156; Chevreul, *Ann. Chim.* 83, 72; abstr. Gilb. 46, 176.) As the ebullition goes on, the solution first turns yellow, in consequence of the formation of the yellow salt B, *b*, but afterwards becomes colourless and yields the required salt. (Chevreul.) If the boiling be not continued long enough to convert all the nitrate into this compound, brick-red needles are obtained contaminated with the salt B, *a*. (Chevreul, Peligot.) —According to Berzelius and Chevreul, the formation of the salt takes place even when the air is completely excluded, and is attended with some evolution of nitric oxide. The reaction is probably, therefore, as follows:

$$5PbO,NO^5 + 11Pb = 4(4PbO,NO^5) + NO^2.$$

According to this view, 11.104 pts. (11 At.) lead re-act upon 5.166 pts. (5 At.) nitrate of lead-oxide = 100 : 138 parts. According to Chevreul, 100 parts of lead-nitrate take up, after long boiling, 135 parts of lead, and, according to Berzelius, 127 parts, which is in accordance with the preceding formula. 830 parts of the neutral salt should, according to the formula, yield 1980 parts of quadrobasic nitrate; Chevreul obtained about 1797 parts.

Pale, flesh-coloured, silky needles united in stellate masses (Chevreul); pale rose-coloured needles, or—if the solution be rapidly cooled—a white powder (Peligot); sometimes also of a light greenish-brown colour. (Bromeis.) This salt has a strong alkaline reaction. In the dry state it is permanent in the air.—Does not give up its water till heated above 100°. Loses a small portion of its acid at 100°, and the whole at a red heat (Chevreul), the decomposition taking place without fusion. (Berzelius.) If part of the oxide be precipitated from the solution by sulphuric or carbonic acid, the liquid turns yellow; from 100 parts of the dissolved salt, carbonic acid gas precipitates 34·8 parts of lead-oxide. (Chevreul.) On dissolving the salt in cold nitric acid or in strong acetic acid, the acid being added gradually so that no heating may take place, a yellow liquid is obtained without any evolution of gas. The acetic acid solution of 100 parts of the salt, shaken up with peroxide of lead, takes up 49·5 parts, the nitrite of lead-oxide being converted into nitrate. (Peligot.) The salt dissolves in 143 parts of water at 25°, in 33 parts of boiling water (Chevreul); in 1250 parts of cold, and 3·45 of boiling water. (Peligot.)

			Berzelius.	Peligot.	Chevreul.
4PbO	448	90·50	90·38	90·52	90·1
NO^3	38	7·68	7·74	9·31	9·9
HO	9	1·82	1·88	1·93	
$4PbO,NO^3 + Aq.$	495	100·00	100·00	101·76	100·0

Peligot found in the salt 3·43 per cent. of nitrogen, which gives 9·31 nitrous acid (14:38 = 3·43 : 9·31).

¶ *b. Terbasic?* Formed, according to Bromeis (*Ann. Pharm.* 72, 50), by boiling the orange-red salt, B, *a*, for several hours in contact with metallic lead. Crystallizes in needles arranged in small concentric groups, sometimes of a brick-red colour, sometimes green and highly lustrous, sometimes exhibiting various shades between these two colours. The amount of lead in this salt was found to vary from 89·57 to 89·34 per cent., that of nitrogen from 3·92 to 3·56, and that of water from 0·93 to 0·35. Bromeis regards it as an anhydrous trinitrite. Gerhardt is of opinion that the variable quantities of water found by Bromeis show that the substance which he examined was not a pure salt.

c. Bibasic.—Formed by boiling the bibasic hyponitrate, B, *b*, for a short time with metallic lead. As the liquid cools, the salt deposits itself upon the hyponitrate in rather long golden-yellow needles, having the form of rectangular prisms terminated with rhombic pyramids, at the extremities of which re-entering angles occur, in consequence of the formation of macle-crystals. (Bromeis.) ¶

				Bromeis.		
2PbO	224	82·65		82·45	—	82·47
NO^3	38	14·02		12·92	—	13·71
HO	9	3·33		3·87	—	3·53
$2PbO,NO^3+Aq.$	271	100·00		99·24	—	99·71

d. Monobasic.—Formed by passing carbonic acid gas through a solution of *a* in hot water—whereby three-fourths of the lead-oxide is precipitated—and leaving the yellow filtrate to evaporate spontaneously (Chevreul), or in vacuo. (Peligot.) If the liquid be heated, nitrous acid is given off. (Chevreul.) Long yellow prisms (Peligot); yellow laminæ. (Chevreul). Very easily decomposed; very soluble in water. (Peligot, *Ann. Chim. Phys.* 77, 87; also *Ann. Pharm.* 39, 338.)

B. Hyponitrate of Lead-oxide, or Lead-hyponitrate.—*a. 7 At. base to 2 At. acid,* or *Quadrobasic?*—1. By boiling the solution of B, *b* with lead-oxide.—2. By boiling 166 parts (1 At.) of lead-nitrate with 156 parts ($1\frac{1}{2}$ At.) lead and a very large quantity of water, and leaving the yellow filtrate to crystallize by cooling. In this process, nitric oxide gas is always evolved. With more than 2 atoms of lead and longer boiling, a colourless solution of quadrobasic nitrite is obtained; and by boiling for a shorter time only, a pale yellow liquid, which on cooling deposits a mixture of the salts B, *a* and B, *b*; these may be separated by boiling water, which extracts the latter. (Peligot.) If the salt be regarded as quadrobasic, the formula of its production may be as follows:

$$3(PbO,NO^5)+5Pb = 2(4PbO,NO^4)+NO^2;$$

With regard to Peligot's assumption that the salt contains $\frac{2}{7}$ At. acid, it is not easy to devise a formula which shall express the mode of formation. Orange-yellow prisms which retain their water till heated above 100°. They dissolve in concentrated acetic acid without evolution of gas, provided the acid be gradually added, so that no heating may take place. The yellow solution of 100 parts of this salt dissolves 27 parts of peroxide of lead, with decoloration of the liquid and formation of nitrate of lead-oxide. By decomposing the salt with baryta-water, we obtain nitrate and nitrite of baryta. The crystals dissolve in 1250 parts of cold and in 34 parts of boiling water. (Peligot.)

	Crystallized. Calculation 1.		Peligot.
$7PbO$	784	86·82	86·64
$2NO^4$	92	10·19	10·41
$3HO$	27	2·99	3·03
$7PbO,2NO^4+3Aq.$	903	100·00	100·08

	Calculation 2.	
$4PbO$	448	87·50
NO^4	46	8·98
$2HO$	18	3·52
$4PbO,NO^4+2Aq.$	512	100·00

Peligot found 3·17 per cent. of nitrogen, which corresponds to 10·41 hyponitric acid. (14 : 46=3·17 : 10·41.)—Berzelius, by boiling 1 part of lead-nitrate with 1½ pt. lead-foil and 50 water, for a long time, and leaving the liquid to cool, obtained sometimes crystals of the pale red salt A, *a*, sometimes brick-red needles. The latter are formed when the boiling is not continued long enough, and consist, according to Peligot, of the pale red salt A, *a*, and the orange-yellow salt B, *a*, which, being soluble in different degrees, may be partly separated by digestion in a quantity of water not sufficient to dissolve the whole. By heating 1 part of lead-nitrate with 1¼ parts (2 At.) of lead and 50 of water, till the lead is completely dissolved, Berzelius obtained a solution which yielded brick-red scales on cooling, and, on evaporating the mother-liquid, the same salt was obtained in brick-red, fern-like tufts, together with the yellow salt B, *b*.

¶ According to Bromeis, there are likewise two other orange-coloured salts formed by boiling lead-nitrate with metallic lead; viz. (1) a compound of a nitrate and a hyponitrate, composed of $4PbO,NO^4+3PbO,NO^5+3HO$, or PbO,NO^4+6PbO,NO^5+3HO; this salt crystallizes in orange-red prisms destitute of lustre; (2) a compound of a nitrite and a hyponitrate, whose formula is $3PbO,NO^3+4PbO,NO^4+3HO$, and which crystallizes in orange-red prisms more lustrous than the salt B, *a*, and having a greater number of facets. The analyses of the three orange-red salts, however, approach so near to each other that it is difficult to believe that the salts are really different, or to attribute the slight variations observed to anything but accidental impurity. The greatest differences in the amount of lead were between 86·02 and 87·72 per cent. (*Comp.* Gerhardt, *Compt. rend. trav. Chim.* 6, 166.) ¶

b. Bibasic.—First obtained by Proust, who regarded it as a nitrate of a suboxide of lead; Berzelius regarded it as a bibasic nitrite of the protoxide. —An aqueous solution of 100 parts (1 At.) of lead-nitrate heated for some hours to a temperature been 70° and 75°, with 78 parts (rather more than 1 At.) of lead-foil, acquires a yellow colour, and deposits yellow scales of this salt as it cools. The action begins between 50° and 55°, but is quicker between 70° and 75°; above 80°, a portion of the salt is decomposed, with evolution of nitric oxide gas. On the first application of the heat, crystals of dinitrate of lead-oxide are likewise deposited. (Berzelius.) Peligot takes 63 parts (1 At.) of lead to 100 parts (1 At.) of the nitrate:

$$PbO,NO^5+Pb=2PbO,NO^4.$$

If, from the presence of too much lead, and from too long boiling, the crystallized salt has become contaminated with orange-yellow scales of the salt B, *a*, Peligot treats it with a small quantity of hot water in

which the yellow salt B, *b* is more soluble, and leaves it to crystallize.—Chevreul boils the aqueous solution of lead-nitrate with excess of lead only till the liquid turns yellow; he states, however, that this process does not yield a pure salt, dinitrate of lead-oxide becoming mixed with it if the boiling be not continued long enough, and quadrobasic nitrite if it be kept up too long. According to Berzelius, 78 parts of lead and 100 of nitrate, yield, after complete solution of the lead, nothing but the yellow salt, quite unmixed with the brick-red salt; according to Peligot, on the contrary, the salt B, *a* becomes mixed with it, even when these proportions are used.—2. If the vapours evolved on heating fuming nitric acid are passed into water containing finely divided lead-oxide, the oxide turns white, and afterwards dissolves completely, forming a deep yellow liquid, which, on evaporation, yields a large quantity of silky scales of nitrite [or hyponitrate?] of lead-oxide, together with a small quantity of nitrate. (Fritzsche, *J. pr. Chem.* 19, 179.)

Yellow, shining laminæ and long flat needles. They blue reddened litmus (Berzelius), have a slightly sweet and astringent taste (Chevreul), and exhibit two axes of double refraction. (Herschel.) The salt does not part with its water till heated above 100°. (Peligot.) Gives off a portion of its acid at 100°, and, at a stronger heat, becomes pasty and darker in colour. (Chevreul.) When heated, it gives off aqueous acid and red vapours, but without fusing. (Berzelius.) Evolves red vapours when heated with stronger acids. (Berzelius, Chevreul.) It dissolves in cold, strong acetic acid, forming a yellow solution, and, without decomposition, if the acid be added gradually so as not to occasion rise of temperature. 100 parts of the salt dissolved in acetic acid dissolve 44 parts of peroxide of lead. On decomposing it with baryta-water, nitrite and nitrate of baryta are obtained. (Peligot.) When the salt obtained by (1) is dissolved in boiling water, yellow laminæ separate out as the liquid cools; the mother-liquid, if evaporated and cooled, yields pale yellow scales and finally white granular crystals together with yellow ones; the mother-liquid, after a portion of the lead-oxide has been precipitated by passing carbonic acid through it, is likewise found to contain nitrate of lead-oxide. (Chevreul.)—The salt dissolves in 80 parts of water at 25°, and in 10·6 parts of boiling water, the yellow solution is rendered turbid by carbonic acid. (Chevreul.) The solution, after very long boiling with lead-oxide, which immediately becomes whitish and flocculent, yields the pale-red salt A, *a*. (Chevreul.)

					Peligot.		Berzelius.		Chevreul.
2PbO	224	....	80·28	....	79·90	....	80·0	....	80·00
NO^4	46	....	16·50	....	16·33	NO^5	13·6	....	17·16
HO	9	....	3·22	....	3·33	....	6·4	....	2·84
$2PbO,NO^4 + Aq.$	279	....	100·00	....	99·56	....	100·0	....	100·00

Peligot found in the salt 4·97 per cent. of nitrogen.

Berzelius decomposed the solution of the bibasic salt B, *b* with a quantity of sulphuric acid just sufficient to precipitate half the lead-oxide, and, by evaporating the yellow filtrate in vacuo, obtained lemon-yellow octohedrons containing 5·7 per cent. of water; these crystals he regarded as mononitrite of lead-oxide. This salt is regarded by Peligot as a mixture of mononitrite and mononitrate of lead-oxide.—Chevreul passed carbonic acid gas through the aqueous solution of the bibasic hyponitrate as long as lead-oxide was precipitated. The filtrate, when evaporated, gave off

red vapours, and yielded white needles of dinitrate of lead-oxide, together with yellowish-white scales containing that salt, and likewise the dinitrite [hyponitrate]; afterwards it yielded yellow octohedrons consisting of dinitrite [hyponitrate] and mononitrate of lead-oxide.

¶. Gerhardt regards the two salts just described, not as hyponitrates, but as double salts composed of nitrates and nitrites. In fact, on adding a solution of nitrate of silver-oxide to a solution of the bibasic salt just described, an immediate precipitate of nitrite of silver-oxide is obtained. —According to this view, the yellow scales first formed by the action of metallic lead on the mononitrate, are composed of dinitrite and dinitrate of lead-oxide;

$$2(2PbO,NO^4,HO) = 2PbO,NO^3,HO + 2PbO,NO^5,HO;$$

and their formation may be represented as follows:

$$2(PbO,NO^5) + 2Pb + 2HO = 2PbO,NO^3,HO + 2PbO,NO^5,HO.$$

If the action of the metallic lead be further continued, a fresh portion of nitrate is de-oxidized, and the result is the orange-yellow salt, which may likewise be regarded as a double salt more basic than the former;

$$7PbO,2NO^4 = 4PbO,NO^3 + 3PbO,NO^5.$$

Finally, by the continued action of the lead, the subnitrate contained in these salts is reduced in its turn, and one or other of the subnitrites A, *a*, or A, *c*, is obtained. (*Compt. rend. trav. Chim.* 6, 168.) ¶

C. Nitrate of Lead-oxide, or Lead-nitrate.—*a. Sexbasic.*—Formed by precipitating the mononitrate with ammonia, and digesting the washed precipitate with that alkali for twelve hours.—White powder, having a slightly astringent taste.—When moderately heated it gives off water, and assumes a yellow colour, but becomes white again on cooling; when ignited it yields yellow pulverulent protoxide of lead. It is nearly insoluble in water. (Berzelius.)

					Berzelius.
6PbO	672	...	91·43	.....	90·80
NO^5	54	...	7·35	.....	7·37
HO	9	...	1·22	.....	1·83
$6PbO,NO^5 + Aq.$	735	...	100·00	.....	100·00

b. Terbasic.—Trinitrate.—Formed by precipitating a solution of the mononitrate with a slight excess of ammonia, digesting in a close vessel, adding more of the mononitrate in drops, digesting again, again dropping in the mononitrate,—and so on, till only a very slight excess of ammonia remains in the liquid, too small to be detected by its odour, and only recognizable by the fumes which it gives with hydrochloric acid. The precipitate is then washed and dried out of contact of air.—White powder. When gently heated, it gives off water and turns yellow, but becomes white again on cooling; when more strongly heated it leaves protoxide of lead in the form of a lemon-yellow powder. Slightly soluble in pure water, but insoluble in water containing in solution various salts which do not exert a decomposing action on the compound. (Berzelius.)

					Berzelius.
6PbO	672	...	83·27	.....	82·98
$2NO^5$	108	...	13·38	.....	13·52
3HO	27	...	3·35	.....	3·50
$2(3PbO,NO^5) + 3Aq.$	807	...	100·00	.....	100·00

c. Bibasic.—Dinitrate.—1. By boiling 1 part of the mononitrate with 1 part of lead-oxide and with water, then filtering, and leaving the solution to crystallize. (Chevreul, *Ann. Chim.* 83, 70.)—2. By heating the mononitrate with white lead and water, filtering at a boiling heat, and leaving the liquid to cool. The carbonic acid is evolved as rapidly as if free nitric acid were present. No salt containing a larger excess of base is formed, even if the white lead is in great excess; for the dinitrate does not decompose white-lead. (Pelouze, *Ann. Chim. Phys.* 79, 107; also *J. pr. Chem.* 25, 486.)—3. By precipitating the mononitrate with a quantity of ammonia not sufficient to throw down the whole of the lead-oxide. (Berzelius, *Gilb.* 46, 142.)—4. When the mononitrate is boiled with zinc-oxide, the bibasic salt separates from the solution. (Persoz, *Ann. Chim. Phys.* 58, 191.)—As the hot aqueous solution cools, the salt separates in white grains and pearly laminæ and needles, having a slightly sweet and astringent taste. These crystals, when gently ignited, leave red-lead, which, at a higher temperature is converted into the yellow protoxide. (Berzelius, *Pogg.* 19, 312.) At 100° they lose but little water, not giving off the whole till heated to between 160° and 190°, and slowly even then. At 200° the salt turns yellow and gives off red vapours. (Pelouze.)—Carbonic acid robs it of half its lead-oxide. (Chevreul.) It is but very slightly soluble in cold water, much more soluble in hot water. (Berzelius, Pelouze.)

	Calculation 1.		Berzelius.	Chevreul.
2PbO	224	80·58	80·5	80·14
NO^5	54	19·42	19·5	19·86
$2PbO,NO^5$	278	100·00	100·0	100·00

	Calculation 2.		Pelouze.
2PbO	224	78·05	78·0
NO^5	54	18·81	19·0
HO	9	3·14	3·1
$2PbO,NO^5$ + Aq.	287	100·00	100·1

According to Berzelius and Chevreul, the crystals are anhydrous, or at least contain nothing but water of decrepitation, which escapes with violence when they are heated; but according to Persoz and Pelouze, they contain 1 atom of crystallization-water.

d. Mononitrate.—Warm dilute nitric acid dissolves lead but slowly, with evolution of nitrous gas; the same compound is obtained by dissolving the oxide.—The salt belongs to the regular system. *Fig.* 1, 2, 4, 13, and 20; also in macle-crystals, like those of spinelle. (Haidinger, *Edinb. J. of Sc.* 1, 102; Wackernagel, *Kastn. Arch.* 5, 295.) Specific gravity, 4·3998. (Karsten.) The crystals exhibit a conchoidal, not a laminar fracture; they are harder than alum, white, with a waxy lustre. (Haidinger.)

			Döbereiner.	Svanberg.	Berzelius.	Chevreul.
PbO	112	67·4	67·6	67·403	67·2225	67
NO^5	54	32·6	32·4	32·597	32·7775	33
PbO,NO^5	166	100·0	100·0	100·000	100·0000	100

The salt decrepitates at a red heat, giving off oxygen gas and hyponitric acid, and leaving protoxide of lead. When it is ignited in a silver crucible, not sufficiently to decompose it, but till it becomes covered with a metallic film, and the mass when cool is boiled with water, the filtrate, after cooling, deposits dinitrate of lead-oxide, and the mother-liquid,

when evaporated deposits metallic lead, while nitrate of lead-oxide remains in solution. (Hess, *Pogg.* 12, 262.) Detonates with brilliant sparks when thrown on red-hot coals; slightly when triturated with sulphur. The inflammability of tinder, blotting paper, &c., is greatly increased by soaking them in a dilute solution of this salt.—It is permanent in the air: dissolves in water producing a great degree of cold. (H. Rose.) One part of the salt dissolves in 1·989 parts of water at 17·5°, forming a liquid of specific gravity 1·3978 (Karsten), in 1·707 water at 22·3°; and 1·585 water at 247°. (Kopp.) The specific gravity of a solution saturated at 8° is 1·372. (Anthon.) Nitric acid precipitates the salt from its aqueous solution. (Braconnot, *Ann. Chim. Phys.* 52, 288.) Insoluble in alcohol. When present in excess, it exhibits a tendency to combine with the insoluble lead-salt formed by precipitation. (Berzelius.)

D. *Boronitride of Lead?*—Cyanide of lead ignited with boracic acid in the manner described (III. 70) yields a mass, which, after washing, gives off ammonia when treated with hydrate of potash.

E. Phosphonitrate of Lead-oxide.—On pouring phosphoric acid into an aqueous solution of lead-nitrate, or evaporating a solution of lead-phosphate in nitric acid, crystalline grains are separated, which may be dried by pressure between bibulous paper: they contain 2 atoms of monophosphate of lead-oxide combined with 1 atom of nitrate; and, when heated, are converted, with evolution of nitrous acid vapours, into triphosphate of lead-oxide. Cold water extracts a small quantity of the nitrate contained in these crystals, and boiling water nearly the whole. (Berzelius, *Ann. Chim. Phys.* 2, 161.) A solution of lead-phosphate in warm nitric acid deposits, on cooling, pure nitrate of lead-oxide crystallized in octohedrons elongated into four-sided prisms. (Dujardin, *J. pr. Chem.* 15, 309.)

¶ F. Azophosphate of Lead-oxide.—$3PbO,P^2NO^5 + 5Aq$.—Formed by adding a soluble lead-salt to a neutral aqueous solution of the salts obtained by treating chlorophosphide of nitrogen (II. 474) with alcohol and ammonia.—White granular powder, which is decomposed by ammonia.—When heated it is decomposed in a similar manner to the iron-salt (q. v.) (Gladstone, *Chem. Soc. Qu. J.* III. 149.) ¶

G. Nitrate of Lead-oxide with Fluoride of Lead.—Fluoride of lead precipitated from a solution of the nitrate by fluoride of sodium contains nitrate of lead in a state of admixture, and difficult to remove by water. (Berzelius.)

H. Plumbite of Ammonia.—1 part of litharge dissolves by digestion in 6 parts of an aqueous solution of caustic ammonia or carbonate of ammonia, forming a deep yellow, non-crystallizable liquid. (Karsten.) The solution is turbid. (Wittstein, *Repert.* 63, 329.)

I. Hyposulphite of Lead-oxide and Ammonia.—Formed by dissolving hyposulphite of lead-oxide in a moderately strong solution of hyposulphite of ammonia—the mixture being shaken and gently heated—and leaving the solution to crystallize by evaporation in the air. At a boiling heat, sulphide of lead would be precipitated; a small quantity of this compound is formed even during spontaneous evaporation.—Trans-

parent and colourless crystals belonging to the right prismatic system. *Fig.* 55 nearly; $u : u' = 104^\circ$; $i : t = 104^\circ, 50'$.—Dissolves easily and completely in cold water. The solution, after standing for a few minutes, or more quickly if heated, deposits hyposulphite of lead-oxide in spangles, which, if heat has been applied, are mixed with sulphide of lead; sulphates added to the solution do not produce an immediate turbidity. (Rammelsberg, *Pogg.* 56, 312.)

	Crystallized.				Rammelsberg.
$2NH^3$	34	....	10·15	.....	9·79
PbO	112	....	33·43	.....	34·45
$3S^2O^2$	144	....	42·99		
5HO	·45	....	13·43		
$2(NH^4O,S^2O^2) + PbO,S^2O^2 + 3Aq.$	335	....	100·00		

K. Sulphate of Lead-oxide and Ammonia.—Sulphate of lead-oxide dissolves abundantly in hot aqueous sulphate of ammonia, in consequence of the formation of a double salt, which, however, separates on cooling. The compound may be prepared by precipitating a moderately strong solution of lead-acetate with dilute sulphuric acid in excess—neutralizing with ammonia—heating nearly to the boiling point till the precipitate is completely re-dissolved—and leaving the solution to crystallize by cooling. If the precipitate does not re-dissolve completely, more sulphate of ammonia must be added. If no crystals separate on cooling, the liquid must be heated again, and sulphuric acid added till turbidity begins to show itself. The double salt appears to form with peculiar facility in a liquid containing a large quantity of acetate of ammonia.—Small, transparent, and colourless crystals.—The salt, when ignited, yields a sublimate of sulphite of ammonia, and a residue of 69·8 per cent. of lead sulphate. In water the crystals immediately become milk-white, the water dissolving out the sulphate of ammonia and, after boiling, leaving 69·2 per cent. of lead-sulphate. (Wöhler & Litton, *Ann. Pharm.* 43, 126.)

					Litton.
NH^4O,SO^3	66	....	30·28	.....	30·3
PbO,SO^3	152	....	69·72	.....	69·8
$NH^4O,SO^3 + PbO,SO^3$	218	....	100·00	.....	100·1

L. Ammonio-iodide of Lead.—100 parts of iodide of lead absorb 7·19 parts (1 At.) of ammonia.—The white compound, when exposed to the air, gives off the whole of its ammonia. Under water, it remains white, but is decomposed into hydriodate of ammonia which dissolves, and protoxide of lead mixed with a small quantity of iodide. (Rammelsberg, *Pogg.* 48, 166.)—Iodide of lead immersed in dilute ammonia turns whitish, and, in a few days, is converted into a white magma, which may be dried in the air without decomposition, but, when heated, is resolved into ammoniacal gas and iodide of lead. (Labouré, *N. J. Pharm.* 4, 328.)

M. Iodide of Lead and Ammonium.—Hydriodate of ammonia in excess forms with nitrate of lead oxide a white precipitate, which is decomposed by a large quantity of water. (P. Boullay.)

N. Ammonio-chloride of Lead.—100 parts of chloride of lead absorb very slowly and with slight intumescence, 9·31 parts ($\frac{3}{4}$ At.) of ammoniacal gas. (H. Rose, *Pogg.* 20, 157.)

O. Chloride of Lead and Ammonium.—*a.* Becquerel obtained this compound crystallized in needles by galvanic action ? (I, 401.)—*b.* An aqueous mixture of chloride of lead and sal-ammoniac is not precipitated by sulphuric acid. (Thénard.)

Lead and Potassium.

A. Alloy of Lead and Potassium.—4 volumes of lead-filings combine at the melting point of lead with 1 volume of potassium, forming a brittle, easily fusible alloy, which exhibits a fine-grained fracture and effervesces strongly with water, but still more with aqueous acids. (Gay-Lussac & Thénard.)—By reducing 100 parts of lead-oxide at a strong red heat with 100 parts of thoroughly burnt or 60 parts of partially burnt tartar, a grey, brittle lead is obtained, which has a fibrous texture and alkaline taste, and, according to Vauquelin (*Schw.* 21, 222), does not effervesce with water; according to Serullas, however (*Ann. Chim. Phys.* 21, 200), it effervesces slowly.

B. Plumbite of Potash.—*Protoxide of Lead with Potash.*—Litharge dissolves in hot potash-ley, forming a yellow liquid which does not crystallize; carbonate of potash acts in a similar manner. (Karsten, *Scher. J.* 5, 575.)—When white lead is boiled with potash-ley, a colourless solution is obtained; and this solution, on cooling, yields small, silver-white, crystalline scales which acquire a grey tarnish by exposure to the air. The remaining liquid forms, on evaporation, a brownish-red, scaly, shining mass, which re-dissolves in water, with the exception of a few shining scarlet scales. Metallic lead is precipitated from the solution by phosphorus and zinc, but not by iron. Tin immersed in a solution of plumbite of potash, throws down all the lead: a case of reciprocal affinity. (Fischer, *Pogg.* 9, 263.)

C. Plumbate of Potash.—*Peroxide of Lead with Potash.*—Formed by fusing peroxide of lead with excess of potash-hydrate in a silver crucible, dissolving in water, and evaporating; the compound is then obtained in definite crystals. It may likewise be formed by fusing potash-hydrate with the yellow protoxide, which is then converted into the peroxide by absorbing oxygen from the air.—This salt dissolves without decomposition in caustic potash, but, in contact with pure water, it turns red and is resolved into aqueous potash and precipitated peroxide of lead. (Fremy, *N. J. Pharm.* 3, 32.)

D. Hyposulphite of Lead-oxide and Potash.—Formed by dissolving hyposulphite of lead-oxide, with agitation, in warm aqueous hyposulphite of potash, and leaving the solution to crystallize by cooling. If the liquid is tolerably concentrated, it solidifies in a white mass, by the formation of extremely delicate, silky needles, which must be pressed to free them from the mother-liquid, that liquid always containing a large quantity of free potash-salt.—The double salt, when heated out of contact of air, gives off sulphurous acid and sulphur, and leaves a residue amounting to 77·39 per cent., and consisting of sulphide of potassium, sulphate of potash, sulphide of lead, and sulphate of lead-oxide. It dissolves in water, with partial separation of hyposulphite of lead-oxide in shining spangles. The solution is not clouded by sulphates, and after

some time only, by sulphuric acid, the precipitate then formed consisting of sulphur and sulphate of lead-oxide. (Rammelsberg, *Pogg.* 56, 310.)

	Crystallized.			Rammelsberg.
2KO	94·4	...	25·62	..... 26·29
PbO	112·0	...	30·40	..... 28·97
$3S^2O^2$	144·0	...	39·09	
2HO	18·0	...	4·89	
$2(KO,S^2O^2)+PbO,S^2O^2+2Aq.$	368·4	...	100·00	

E. Sulphate of Lead-oxide and Potash. — Precipitated when sugar-of-lead is mixed with sulphate of potash. It appears to contain sulphate of lead-oxide and sulphate of potash in equal numbers of atoms; but the longer it is boiled with water, and the greater quantity of water present, the greater is the quantity of sulphate of potash dissolved out of it. (Trommsdorff, *Taschenb.* 1825, 1.)

F. Iodide of Lead and Potassium.—*a.* $2KI,PbI^2$.—Separates in yellowish, silky crystals, on pouring a solution of lead-nitrate into an excess of concentrated aqueous iodide of potassium.

				Boullay.
2KI	330·4	...	58·96	 64
PbI	230·0	...	41·04	 36
2KI,PbI	560·4	...	100·00	 100

b. 2KI,3PbI.—1. The mother-liquid poured off from *a* yields yellow prisms after a few days.—2. The mother-liquid poured off from the yellow prisms and mixed with alcohol, deposits white crystals having a silky lustre.—If water be added instead of alcohol, yellow iodide of lead is separated at first, but it is soon converted into the white salt *b*.—3. When nitrate of lead-oxide is poured into a less concentrated solution of iodide of potassium, a yellow precipitate is formed, but is soon converted into white silky needles, which thicken the liquid. On heating the mixture, yellow iodide of lead is formed, which still retains the form of the needles, and, on cooling, is reconverted into white iodide of lead and potassium. (P. Boullay.)—This salt is formed, together with carbonate of lead-oxide, on boiling iodide of lead with a concentrated solution of carbonate of potash. (Berthemot, *J. Pharm.* 13, 311.) Becquerel obtained it, by electrolytic action, in white silky needles. (I, 401.)—The needles are permanent in the air. When heated, they turn yellow, give off a small quantity of water, and fuse into a red liquid, which, on cooling, solidifies in a yellow mass. Heated with sulphuric acid, they deposit, first iodide of lead, and then sulphate of lead-oxide. Water separates iodide of lead from the crystals, dissolving out the iodide of potassium, together with a small quantity of iodide of lead, which, however, when a large quantity of water is used, does not exceed a mere trace. Cold alcohol has no action on the crystals; hot alcohol leaves iodide of lead undissolved and deposits the salt *b* on cooling, iodide of potassium remaining in solution. (Boullay, *J. Pharm.* 12, 639; also *Ann. Chim. Phys.* 34, 366.)

					Boullay. (1)		(2)		(3)
2KI	330·4	...	32·38	.....	30·5	...	31	...	30·25
3PbI	690·0	...	67·62	.....	69·5	...	69	...	69·75
2KI,3PbI	1020·4	....	100·00	.....	100·0	...	100	...	100·00

The crystals (3) likewise contain 3 per cent. of water. (Boullay.)

G. Bromide of Lead and Potassium.—When concentrated solutions of nitrate of lead-oxide and bromide of potassium, the latter somewhat in excess, are mixed, filtered, and evaporated, small octohedrons are produced, soluble without decomposition in a very small quantity of water, but decomposed by a larger quantity, with separation of bromide of lead. (Löwig.)

	Crystallized.			Löwig.	Or:			
K.....	39·2	...	13·06	... 12·90	KBr	117·6	...	39·2
Pb	104·0	...	34·66	... 36·38	PbBr	182·4	...	60·8
2Br	156·8	...	52·26	... 50·72				
KBr,PbBr	300·0	...	100·00	... 100·00		300·0	...	100·0

Lead and Sodium.

A. Alloy of Lead and Sodium.—4 volumes of lead-filings heated with 1 volume of sodium to the melting point of lead, fuse with evolution of heat, but not of light, and form a bluish-grey, slightly extensible, fine grained alloy, which melts at the same temperature as lead, oxidizes in the air, and effervesces slightly in water, but strongly in aqueous acids.—3 volumes of lead-filings form, with 1 volume of sodium, a brittle, easily oxidable alloy. (Gay-Lussac & Thénard.) An alloy may also be formed by igniting lead with charred soap.

B. Plumbite of Soda.—Litharge dissolves in a boiling aqueous solution of caustic soda or carbonate of soda, forming a yellow liquid. (Karsten.)

C. Plumbate of Soda.—Analogous to plumbate of potash. (Fremy.)

D. Carbonate of Lead-oxide and Soda.—When nitrate of lead-oxide is precipitated by carbonate of soda, the precipitate boiled in the alkaline liquid, and afterwards washed and dried at 160°, this precipitate evolves, on ignition, 15·185 per cent. of carbonic acid, and is therefore composed of $NaO,CO^2+4(PbO,CO^2)$.—(Berzelius, *Pogg.* 47, 199.)

E. Sulphide of Lead and Sodium.—20 parts of lead-sulphate heated to whiteness in a charcoal crucible with 10 parts of dry sulphate of soda, yield 3·5 parts of metallic lead, and 19 parts of a metallic sulphide containing from 20 to 25 per cent. of sulphide of sodium. Sulphide of lead and sodium is a shining, lead-grey, brittle substance, exhibiting a close fracture. Water dissolves out the sulphide of sodium from it, and leaves a compound of one atom of sulphur with more than one atom of lead. (Berthier, *Ann. Chim. Phys.* 22, 215.)

F. Hyposulphite of Lead-oxide and Soda.—Formed by adding acetate of lead-oxide to aqueous hyposulphite of soda, as long as the precipitated hyposulphite of lead-oxide re-dissolves on agitation—precipitating the double salt from the filtrate with alcohol—and washing the precipitate with alcohol. It may also be obtained by dissolving chloride of lead in hyposulphite of soda.—The precipitate becomes crystalline after awhile. It dissolves sparingly in water, but very freely in aqueous acetate of soda. (Lenz, *Ann. Pharm.* 40, 98.) It resembles the potash-salt in every respect. (Rammelsberg, *Pogg.* 56, 311.)

					Lenz.
$2NaO$	62·4	...	19·60	.....	19·09
PbO	112·0	...	35·18	.....	35·84
$3S^2O^2$	144·0	...	45·22	.....	46·11
$2(NaO,S^2O^2) + PbO,S^2O^2$	318·4	...	100·00	.....	101·04

G. Sulphate of Lead-oxide and Soda.—Sulphate of lead-oxide and sulphate of soda in equal numbers of atoms fuse at a red heat, forming a liquid as thin as water, and yield, on cooling, an opaque mass, having an uneven, non-crystalline fracture. (Berthier, *Ann. Chim. Phys.* 38, 256.)

H. Iodide of Lead and Sodium.—Becquerel obtained this compound, by the electrolytic method, in needles having a silky lustre. (I, 401.)

I. Bromide of Lead and Sodium.—May be prepared in the same way as the potassium compound. Crystallizes in prisms. Decomposible by water. (Löwig.)

K. Chloride of Lead and Sodium.—Obtained by Becquerel in tetrahedrons, by the electrolytic method. (I, 401.)

Lead and Barium.

A. Plumbite of Baryta.—Boiling baryta-water forms with lead-oxide a deep yellow solution, which, on evaporation, leaves its two constituents separate [in the form of carbonates ?]. (Karsten.)

B. Sulphide of Lead and Barium.—15 parts of sulphide of lead heated to whiteness in a charcoal crucible with 15 parts of sulphate of baryta yield 17 parts of sulphide of lead and barium, sulphide of lead being sublimed and a small quantity of metallic lead reduced.—This compound is of a dingy red colour, without metallic lustre, and of shining laminar fracture. Water extracts the sulphide of barium and leaves 10 per cent. of sulphide of lead. (Berthier.)—When sulphide of lead and sulphide of barium, in equal numbers of atoms, are heated to whiteness in a charcoal crucible, the greater part of the lead-sulphide volatilizes, and there remains a well fused, blistered mixture, having a brown-red colour and waxy lustre, and yielding a red powder. (Fournet.)

C. Hyposulphite of Lead-oxide and Baryta.—Hyposulphite of lead-oxide and potash, mixed with acetate of baryta, throws down, after a few minutes, a precipitate consisting of the barytic double salt. The precipitate, however, is mixed with free hyposulphite of baryta, because at the solution of the potassic double salt contains free hyposulphite of of potash. The digestion of hyposulphite of baryta with water and hyvibles sulphite of lead-oxide does not form a solution. (Rammelsberg, Annalen 56, 313.)

D. Chloride of Lead and Barium.—Obtained by the [illegible]-oxide yield method in crystals having a silky lustre. (Becquerel, I. 4[illegible] [illegible]llow glass, of [illegible]ate of lead-oxide [illegible]rongly tarnished by

LEAD AND STRONTIUM.

HYPOSULPHITE OF LEAD-OXIDE AND STRONTIA.—Hyposulphite of lead-oxide dissolves abundantly in aqueous hyposulphite of strontia; the solution, however, yields no crystals, but deposits a syrup on the addition of alcohol. (Rammelsberg.)

LEAD AND CALCIUM.

A. PLUMBITE OF LIME.—Heated lime-water dissolves lead-oxide, forming a yellow solution. On evaporating the liquid, the plumbite of lime crystallizes in small spiculæ, which have a caustic taste, and are slightly soluble in water, forming a solution which blackens wool, nails, and horn. (Karsten, *Scher. J.* 5, 575; Berthollet, *Ann. Chim.* 1, 52.)

B. CARBONATE OF LEAD-OXIDE AND LIME.—*Plumbo-calcite.*—Obtuse rhombohedrons, *Fig.* 141; $r^3 : r^5 = 104° 53'$ (Brewster). Specific gravity 2·824. Softer than calcspar; transparent, with a pearly lustre.—Contains 92·2 per cent. of carbonate of lime, 7·8 p. c. carbonate of lead-oxide, and a trace of ferric oxide. Decrepitates in the fire, and by continued ignition acquires a brownish or reddish colour. With carbonate of soda on charcoal before the blowpipe, it yields a white enamel but no globules of lead. (Johnston, *N. Edinb. J. of Sc.* 6, 79; also *Pogg.* 25, 312.)

C. HYPOSULPHITE OF LEAD-OXIDE AND LIME.—From a solution of hyposulphite of lead-oxide in aqueous hyposulphite of lime, which is not rendered turbid by the addition of sulphates, alcohol throws down the double salt in white crystalline granules, partially decomposible by water. (Rammelsberg.)

	Crystallized.			Rammelsberg.
2CaO	56	....	16·09	..... 17·00
PbO	112	....	32·18	..... 30·29
$3S^2O^2$	144	....	41·38	
4HO	36	....	10·35	
$2(CaO,S^2O^2) + PbO,S^2O^2 + 4Aq.$	348	....	100·00	

D. PHOSPHATE OF LEAD-OXIDE AND LIME WITH CHLORIDE OF LEAD. —*Nussierite.*— This mineral occurs in connexion with Pyromorphite (p. 149). Very obtuse rhombohedrons. Specific gravity 5·0415. Yellowish, greenish, or greyish, with a faint waxy lustre. After fusion before the blowpipe, it solidifies into a whitish, angular enamel. Forms a yellowish glass with borax. Dissolves readily and without effervescence in nitric acid. Contains: PbCl 7·65,—CaO 12·30,—PbO 46·50,—FeO 2·44,—cPO^5 19·80,—AsO^5 4·06,—quartz 7·20 (less 0·05). (G. Barel, *Ann. Chim. Phys.* 62, 217; also *J. pr. Chem.* 10, 10.)

acet.

precip. SULPHATE OF LEAD-OXIDE WITH FLUOR-SPAR.—*a.* One atom of tating tr with one atom of lead-sulphate fuses very easily to a thin precipitate ch, on cooling, yields a dense, spongy mass, of uneven, non- of lead in lacture.—*b.* 1 At. fluor-spar with 2 At. lead-sulphate: Fuses after awhile. and forms as thin a liquid as the above, and yields a *acetate of soda.* (white, stony mass.—*c.* 1 At. fluor-spar with 4 At. *salt in every respect.* s less completely, and forms yellowish, blistered,

crumbling, granular, but not crystalline mass.—*d.* 1 At. fluor-spar, 1 At. lead-sulphate, and 1 At. lime: This mixture yields sulphate of lime and uncombined lead-oxide; fuses very easily to a very thin liquid, which, on cooling, forms a pale-grey, crystalline-laminar mass.—*e.* 4 parts of fluor-spar, 5 of heavy-spar, 6 of ignited gypsum, and 5 of lead-sulphate: Fuses perfectly at an incipient white heat and forms a thin liquid. Dense white enamel, having an uneven fracture. (Berthier, *Ann. Chim. Phys.* 43, 298.)

Lead and Aluminum.

Phosphate of Lead-oxide with Hydrate of Alumina.—*Hydrous Aluminate of Lead, Plombgomme, Bleigummi.*—Amorphous; harder than fluor-spar; of conchoidal fracture; yellowish-brown; translucent. When heated, it decrepitates strongly, gives off water, turns white, swells up, and fuses partially if urged by a strong blast. With carbonate of soda on charcoal, it yields globules of lead. Assumes a blue colour when ignited with nitrate of cobalt. Dissolves in nitric acid. (Berzelius, *Schw.* 27, 65; Jahresber, 21, 214; Dufrénoy, *Ann. Chim. Phys.* 59, 440; also *J. pr. Chem.* 7, 163; Damour, *Ann. Mines. Ser.* 3, 17, 191; also *J. pr. Chem.* 21, 126.)

	Plombgomme.			Berzelius. Huelgoet.	Berzelius. Huelgoet.	Dufrénoy. Nussière.
$3PbO$	336·0	38·28		35·10	40·14	43·42
PO^5	71·4	8·14		8·06		1·89
$6Al^2O^3$	308·4	35·13		34·32	37·00	34·23
$18HO$	162·0	18·45		18·70	18·80	16·14
CaO				0·80		
Fe^2O^3				0·20	1·80	
MnO						
$PbCl$				2·27	SeO^2 0·60	2·11
SO^3				0·30	SO^2 0·20	
$6(Al^2O^3,3HO)+3PbO,PO^5$	877·8	100·00		99·75	98·54	97·79

Lead and Silicium.

A. Silicide of Lead.—The two metals fuse together before the blowpipe and form a malleable alloy, which, when dissolved in acids, leaves a residue of silica. (Berzelius, *Pogg.* 1, 220.)

B. Silicate of Lead-oxide, or Lead-silicate.—*a.* Silica fuses with lead-oxide to a yellow-glass. Glass formed of equal parts of lead-oxide and silica does not become dull in the air of a town (as from the action of sulphuretted hydrogen, which might form sulphide of lead); nor even when 3 parts more of lead-oxide are added to 8 parts of the glass; but the tarnishing takes place if 8 parts of the glass are fused with 1 part of potash. (Faraday, *Pogg.* 18, 568.) Lead-oxide attacks earthen crucibles when fused in them.—*b.* Silico-fluoride of lead yields with ammonia a precipitate of lead-silicate.

C. Borosilicate of Lead-oxide.—112 parts of lead-oxide yield with 16 parts of silica and 24 of boracic acid a yellow glass, of specific gravity 6·44, which fuses less easily than borate of lead-oxide (p. 128) but more easily than flint-glass, and is strongly tarnished by immersion in hydrosulphuric acid gas. (Faraday.)

D. Silicofluoride of Lead.—PbF,SiF^2.—A solution of lead-oxide in hydrofluosilicic acid dries up to a translucent gum, having the taste of other lead-salts, and re-dissolving perfectly in water. (Berzelius.)

E. Silicate of Lead-oxide and an Alkali.—*a. Lead-glass.*—Lead-oxide forms, with silica and potash or soda, a vitreous mass, which is distinguished from other kinds of glass by its greater density, refracting power, softness, and fusibility, and has so much the greater tendency to become tarnished in impure air with sulphide of lead, as it is richer in lead-oxide and more finely divided. A large quantity of lead-oxide colours it yellow, and the presence of metallic lead (or the suboxide) gives it a green tint: *Flint-glass, Mainzer Fluss, Glazing.* (III. 380, 381.)

b. Containing a larger proportion of potash.—The aqueous solution of soluble glass (III. 371) if agitated with lead-oxide, takes up a portion of that substance, slowly at ordinary temperatures, but more quickly when heated, and is thereby converted into a stiff jelly, which, when exposed to the air, dries up to an opalescent mass. (Fuchs, *Kastn. Arch.* 5, 401.)

F. Silicate of Zirconia and Lead-oxide.—*a.* $2PbO,2ZrO,SiO^2$.—91·8 parts (1 At.) of zircon fuse with 224 parts (2 At.) of lead-oxide, forming a yellow, translucent, dense mass, having a waxy lustre and resembling gamboge.—*b.* $PbO,2ZrO,SiO^2$.—91·8 parts (1 At.) of zircon soften when heated with 112 parts (1 At.) of lead-oxide and form a stiff paste, which solidifies in a homogeneous, waxy, opaque mass. Both these compounds are easily attacked by acids. (Berthier, *Ann. Chim. Phys.* 59, 193.)

Lead and Titanium.

Fluoride of Titanium and Lead.—Small colourless crystals, which taste sour at first, but afterwards sweet and astringent, and dissolve easily in water without decomposing. (Berzelius, *Pogg.* 4, 5.)

Lead and Tantalum.

Fluoride of Tantalum and Lead.—Difficultly soluble in water. (Berzelius.)

Lead and Tungsten.

A. Tungstide of Lead.—Formed by exposing a mixture of lead and tungstic acid to a very intense heat in a charcoal crucible.—Dark brown, with a faint lustre, spongy, and very ductile. (De Luyart.)

B. Tungstate of Lead-oxide, or Lead-tungstate.—*a. Monotungstate.*—Found native, as *Scheelitine.* Belongs to the square prismatic system; isomorphous with tungstate of lime (Kobell, *Schw.* 64, 410), and with molybdate of lead-oxide (A. Levy, *Ann. Phil.* 28, 364; also *Pogg.* 8, 513); *Figs.* 24, 28, 32, 35, with truncation of the edges between e and e'; $e : e'' = 131° 30'$; $e : e'' = 154° 36''$ (Levy). Cleavage parallel to p and e. (Breithaupt.) Specific gravity 8·0. Harder than gypsum. Colourless or brownish-white; transparent or translucent, with a waxy lustre. Fuses before the blowpipe, covering the charcoal with a deposit of lead-

oxide, and, on cooling, solidifies in the form of a dark crystalline globule. With borax it yields a colourless glass in the outer flame, and in the inner, a yellowish glass, which becomes grey and opaque on cooling; if the fusion with borax be continued for a longer time, lead is volatilized, and a clear dark-red glass is formed. With microcosmic salt, this mineral forms a colourless glass in the outer flame, and a blue glass in the inner. With carbonate of soda on charcoal, it yields globules of lead. Dissolves in nitric acid, with separation of yellow tungstic acid.

When a lead-salt is precipitated with monotungstate of potash, a white anhydrous powder is obtained, which when heated, first turns grey and then yellowish, fuses at a red heat, and solidifies in a crystalline mass on cooling. Insoluble in water and cold nitric acid, but soluble in caustic potash. (Anthon, *J. pr. Chem.* 9, 342.)

b. Bitungstate.—Formed by precipitating nitrate of lead-oxide with bitungstate of ammonia.—White powder, insoluble in water. (Berzelius.)

	Monotungstate.			Lampadius. *native.*	Anthon. *artificial.*
PbO	112	48·28		48·25	48·4
WO^3	120	51·72		51·75	51·6
PbO,WO^3	232	100·00		100·00	100·0

	Bitungstate.			Berzelius.
PbO	112	31·8		28·58
$2WO^3$	240	68·2		71·42
$PbO,2WO^3$	352	100·0		100·00

D. Sulphotungstate of Lead,—PbS,WS^3. By mixing sulphotungstate of potassium with a lead-salt. Dark brown precipitate, almost black when collected. If a lead-salt be precipitated by the compound of sulphotungstate of potassium with tungstate of potash (IV, 40), the resulting precipitate is of a dingy yellow colour. (Berzelius.)

Lead and Molybdenum.

Molybdide of Lead.—Lead alloyed with a small quantity of molybdenum is whiter than pure lead, hard, and somewhat malleable; with a larger quantity of molybdenum it forms a black, brittle mass. (Hjelm.)

B. Molybdate of Lead-oxide, or Lead-molybdate.—Occurs in the form of *Yellow Lead-ore, Melinose* (*Gelbbleierz*). Prepared artificially by precipitating nitrate of lead-oxide with monomolybdate of ammonia. The native variety belongs to the square prismatic system. *Figs.* 23, 24, 25, 27*, 28, 33, and other forms. $e:e''=76° 40'$; $e:e'=128°$; $p:e=141° 40'$; $e:r=128° 20'$; $p:a=140° 1'$. Cleavage parallel to *p*, *e*, and *r*. (Hauy.) Specific gravity=6·76. (Mohs.) Harder than gypsum; yellow, translucent, with a waxy lustre. Decrepitates strongly when heated and assumes a darker colour, which, however, disappears on cooling; fuses to a yellow mass. When fused upon charcoal before the blowpipe, it sinks into the charcoal, leaving globules of lead, while the charcoal becomes impregnated with molybdenum and molybdide of lead. It dissolves in carbonate of soda, and with that substance sinks into the charcoal, leaving

* In fig. 27, read *a* instead of *e*.

globules. Dissolves easily in borax; the glass formed in the outer flame is slightly coloured, and that obtained in the inner flame is clear while hot, but in cooling suddenly becomes dark and opaque. Dissolves readily in microcosmic salt, forming a glass which is green if the quantity of mineral dissolved in it is small, but black and opaque if the quantity is larger. (Berzelius.) Dissolves in heated nitric acid, with separation of yellowish-white nitrate of molybdic acid. It is decomposed by sulphuric acid. Strong hydrochloric acid dissolves it, producing a green solution, and forming chloride of lead, which separates more completely on the addition of alcohol. Soluble in caustic potash, but not in water.

				Hatchett. Bleiberg.	Göbel. Bleiberg.	Melling. Bleiberg.	Klaproth. Bleiberg.	Berzelius. *artif.*
PbO	112	60·87		58	59·0	61·90	64·42	60·81
MoO^3	72	39·13		38	40·5	40·29	34·25	39·19
Fe^2O^3				3				
PbO,MoO^3	184	100·00		99	99·5	102·19	98·67	100·00

According to Rammelsberg, the native molybdate of lead-oxide from Bleiberg appears to contain a small quantity of vanadiate. The red-coloured molybdate from Retzbanya was declared by Johnston (*Phil. Mag. J.* 12, 387) to be chromate of lead-oxide; and since, according to Brooke's statement, it exhibited the crystalline form of the molybdate, Johnston concluded that chromate of lead-oxide must be dimorphous. According to G. Rose, however (*Pogg.* 46, 639), the red ore in question is molybdate of lead-oxide, with which perhaps a small quantity of chromate may be mixed. If this be the case, the dimorphism mentioned at page 102, vol. I, does not exist. Boussingault (*Ann. Chim. Phys.* 45, 325) examined an impure ore from Pamplona containing excess of lead-oxide.

C. Sulphomolybdate of Lead.—Black precipitate, remaining black even when dry, and producing a lead-grey streak.

D. Persulphomolybdate of Lead.—Dark-red powder. (Berzelius.)

Lead and Vanadium.

Vanadiate of Lead-oxide, or Lead-vanadiate.—*a. Monovanadiate.*—Formed by precipitating nitrate of lead-oxide with an alkaline monovanadiate. Also by precipitating sugar-of-lead with an alkaline bivanadiate, in which case acetic acid is set free in the liquid. The precipitate, which is yellow at first, becomes white and less bulky in the course of 24 hours. It fuses easily, forming a reddish-yellow liquid, and on cooling solidifies in a yellow mass. It is decomposed by fusion with bisulphate of potash; not quite completely by oil of vitriol; neither is it decomposed by boiling with carbonate of potash. Dissolves slightly in water forming a yellow solution; and is easily soluble in slightly warmed nitric acid, even when dilute. The solution in strong nitric acid, when heated to the boiling point, deposits a brown powder containing oxide of lead with a large excess of vanadic acid. (Berzelius.)

b. Bivanadiate.—Nitrate of lead-oxide forms with bivanadiate of potash, an orange-yellow precipitate, which fuses readily, and, on cooling, crystallizes in a red mass. Gives up half its acid to boiling carbonate of potash. Slightly soluble in water, to which it imparts a yellow colour. (Berzelius.)

Vanadite.—Ore from Beresow. Regular six-sided prisms. Sometimes one part of such a prism consists of brown Vanadite and the other of Pyromorphite, a structure which would seem to indicate isomorphism, were it not that vanadic acid and phosphoric acid do not agree in stoïchiometric composition. Brown, with a strong lustre. Decrepitates strongly, and fuses on charcoal to a bead which yields metallic lead, with emission of sparks, and forms a yellow film on the charcoal. The solution of the mineral in microcosmic salt yields in the outer flame a reddish-yellow glass, which becomes yellowish-green on cooling,—and in the inner flame a glass which exhibits the beautiful green of chromium. Dissolves easily in nitric acid, and nitrate of silver throws down a large quantity of chloride of silver from the solution. *The ore from Zimapan* behaves in a similar manner. (G. Rose, *Pogg.* 29, 455.)—*Ore from Wanlockhead.* Specific gravity 6·99....7·23. Colour varying from yellow to brown; opaque with a waxy lustre. Decrepitates when ignited and assumes a red colour which again becomes yellow on cooling. If kept in a state of fusion for a short time only, it solidifies in a yellow mass; but by longer fusion it is converted into a spongy, steel-grey mass, which, when ignited upon charcoal, immediately yields globules of lead. Fuses readily upon charcoal, exhaling an odour of arsenic, yields globules of lead, and after fusion for some time in the inner flame, likewise yields a steel-grey, very fusible slag, which exhibits the reactions of chromium. When treated with nitric acid, it first yields up the lead-oxide, so that the fragments become covered with a red coating of vanadic acid, which is afterwards likewise dissolved and imparts a yellow colour to the liquid. With hydrochloric or sulphuric acid it forms a green solution, chloride of lead or sulphate of lead-oxide being separated. (Johnston, *N. Ed. J. of Sc.* 5, 166; also *Schw.* 63, 119.)

					Berzelius. Zimapan.		Damour. Of unknown origin.
PbCl	139·4	....	9·78	....	9·94	....	8·89
9PbO	1008·0	....	70·73	....	68·00	....	63·72
$3VO^3$	277·8	....	19·49	....	21·34	....	15·86
ZnO		....		....		....	6·34
Fe^2O^3		....		....	0·72	CuO	2·96
HO		....		....		....	3·80
$PbCl+3(3PbO,VO^3)$?	1425·2	....	100·00	....	100·00	....	101·57

Lead and Chromium.

Chromate of Lead-oxide, or Lead-chromate.—*a. Dichromate. Chrome-red.*—1. Formed by boiling the pulverized monochromate with dilute potash-ley (Grouvelle), or with water and carbonate of lead-oxide (Dulong), or with ⅔ pt. lead-oxide and water (Badams, *Ann. Phil.* 25, 303; also *Pogg.* 3, 221): or by boiling it for some time with monochromate of potash, which is thereby converted into the bichromate. (Berzelius.)—2. By boiling lead-oxide or its carbonate with an aqueous solution of monochromate of potash. (Dulong, *Schw.* 5, 384.)—3. By mixing a solution of lead-oxide in caustic soda with chromate of potash, placing the mixture in a basin, and covering it with a bell-jar, under which carbonic acid gas is slowly evolved by the action of sulphuric acid on pieces of marble. As the soda becomes saturated with carbonic acid, the salt crystallizes in orange-yellow needles. (Hayes.) By mixing a very dilute solution of nitrate of lead-oxide with chromate of potash containing a considerable

laminæ of the salt *a*. (Wöhler & Liebig.)—Heated sulphuric acid decomposes the salt, with formation of lead-sulphate; heated hydrochloric acid forms a green solution of chromic hydrochlorate, with separation of chloride of lead, and evolution of chlorine gas. If the hydrochloric acid is mixed with alcohol, the formation of the green solution is attended with the evolution of hydrochloric ether. The salt is insoluble both in pure water and in water containing sal-ammoniac; but, according to Conybeare (*N. Edinb. Phil. J.* 7, 109), it dissolves sparingly in water containing chromate ef potash.

Lead and Uranium.

Uranate of Lead-oxide.—$PbO, 2U^2O^3$.—1. By precipitating an aqueous mixture of lead-nitrate and uranic nitrate with ammonia. (Arfvedson, *Pogg.* 1, 258.)—2. By boiling freshly precipitated lead-carbonate with uranic acetate till the former acquires a yellowish-red colour, and afterwards boiling with fresh uranic acetate. (Wertheim, *J. pr. Chem.* 29, 228.)—3. By precipitating basic lead-acetate with uranic nitrate. (Persoz, *Ann. Chim. Phys.* 56, 335.)—Yellowish-red substance, which when ignited, first becomes brown-red and then again yellowish-red. If heated in a pottery-furnace, it acquires a straw-yellow colour, without any reduction. (Wertheim.) Becomes cinnamon-coloured by ignition. When ignited in a current of hydrogen gas, it gives off 6·34 per cent. of oxygen and yields a dark brown powder [a mixture of uranous oxide and lead], which, if exposed to the air after perfect cooling, takes fire and is reconverted with incandescence, into uranate of lead-oxide (Arfvedson):

$$PbO,2U^2O^3 + 3H = Pb + 4UO + 3HO.$$

After ignition, it is very difficultly soluble in acetic acid. (Wertheim.)

					Wertheim.
PbO	112	....	28	.....	28·79
$2U^2O^3$	288	....	72	.....	71·02
$PbO,2U^2O^3$	400	....	100	.....	99·81

Lead and Manganese.

A. Permanganate of potash gives with nitrate of lead-oxide a brown precipitate, which dissolves completely in cold nitric acid, forming a brown solution. (Forchammer.)

B. Manganous oxide fuses with lead-oxide, forming a green glass, which, when it takes up more oxygen from the air, assumes a brown-red colour. (Berthier.)

Lead and Arsenic.

A. Arsenide of Lead.—1. Melted lead takes up one-sixth of its weight of arsenic, without visible combustion, thereby becoming brittle, and acquiring a laminar texture. *Lead-shot* are made of lead with a very small quantity of arsenic.—2. Arseniate of lead-oxide reduced in a charcoal crucible yields a semi-ductile alloy, which exhibits a white fracture, and gives up all its arsenic if exposed for some time to a white heat in a charcoal crucible. (Fournet.)

B. ARSENITE OF LEAD-OXIDE OR LEAD-ARSENITE.—*a. Bibasic.*—1. By precipitating basic acetate of lead-oxide with ammonia saturated with arsenious acid.—White powder, which, when heated, gives off its combined water, and fuses to a yellowish, idio-electric, vitreous mass. (Berzelius, *Ann. Chim. Phys.* 11, 233.)—2. When arsenious acid vapour is passed over ignited lead-oxide, it is rapidly absorbed, the oxide fuses and becomes red-hot, and, on cooling, solidifies to a sulphur-yellow enamel or glass, which fuses readily and is not decomposed, even at a bright-red heat. No arsenic or lead is reduced to the metallic state, unless either the oxide of lead or the arsenious acid is in excess; when the proper proportions are observed, nothing but [bibasic?] arsenite of lead-oxide is produced. (Simon, *Pogg.* 40, 336.)—Arsenite of lead-oxide is not soluble either in aqueous ammonia, or in arsenite of ammonia or other ammoniacal salts. (Wittstein.)

				Berzelius.
$2PbO$	224	69·35		68·7
AsO^3	99	30·65		31·3
$2PbO,AsO^3$	323	100·00		100·0

b. Monobasic.—By precipitating a monobasic lead-salt with aqueous ammonia, which has been saturated, while warm, with arsenious acid.—White powder, which, when triturated in a mortar, becomes more strongly electrical than sulphur. When heated, it fuses to a yellowish, strongly idio-electric glass, and a small portion of the arsenious acid and combined water are given off. Slightly soluble in water. (Berzelius.)

				Berzelius.	
				earlier.	*later.*
PbO	112	53·08		54·333	52·644
AsO^3	99	46·92		45·667	47·356
PbO,AsO^3	211	100·00		100·000	100·000

C. ARSENIATE OF LEAD-OXIDE OR LEAD-ARSENIATE.—*a. Terbasic.*—1. By precipitating neutral lead-acetate with diarseniate of soda, in which case free acetic acid remains in the liquid, or by precipitating any lead-salt with diarseniate of soda in excess, whereby monoarseniate of soda is produced. (Mitscherlich.)—When neutral lead-acetate is precipitated by trisarseniate of soda, the precipitate contains more than 3 atoms of base if the lead-salt is in excess; but if a solution of 1 part of lead-acetate be added to a solution of 1 part of trisarseniate of soda (in which case the latter will predominate), the precipitate will consist of terbasic salt. (Graham, *Pogg.* 32, 51.)—2. By digesting *b* with ammonia. (Berzelius.) White, fusible powder. (Berzelius.) When raised to a low red heat, at which it neither fuses nor bakes together, it acquires a transient yellow colour. (Graham.) Insoluble in water; likewise insoluble in aqueous ammonia and its salts. (Wittstein.)

				Berzelius (2).		Graham (1).
$3PbO$	336	74·5		74·75		74·33
AsO^5	115	25·5		25·25		25·67
$3PbO,AsO^5$	451	100·0		100·00		100·00

b. Bibasic.—Formed slowly by the action of air and aqueous arsenic acid upon lead; precipitated on mixing aqueous hydrochlorate or nitrate of lead-oxide with arsenic acid,—or on gradually dropping diarseniate of ammonia, potash, or soda, into an excess of mononitrate of lead-oxide.

(Berzelius, Mitscherlich.) Fuses more easily than *a*, forming an opaque mass; crystallizes on cooling, according to Mitscherlich, but according to H. Rose it does not. On charcoal in the inner flame, it exhales an odour of arsenic, and yields globules of lead. (H. Rose.) Dissolves in hydrochloric or nitric acid, but not in water or acetic acid.

			Berzelius.	Thénard.	Chenevix.
2PbO	224	66·08	65·86	64·3	63
AsO^5	115	33·92	34·14	35·7	33
HO					4
$2PbO, AsO^5$	339	100·00	100·00	100·0	100

D. Sulpharsenite of Lead.—$2PbS, AsS^3$.—Red-brown precipitate, black after drying, and yielding a brown powder; fuses readily without giving off sulphide of arsenic, and solidifies to a metal-grey mass, having a shining, crystalline fracture, and yielding a grey powder. (Berzelius, *Pogg.* 7, 147.)—10 parts of galena heated to whiteness in a charcoal crucible with 5 parts of orpiment, volatilize, leaving only 1 part of ductile lead; hence orpiment favours the volatilization of sulphide of lead. (Fournet.)

E. Sulpharseniate of Lead.—Lead-salts give dark brown precipitates with the aqueous solution of bibasic sulpharseniate of sodium, and red with the terbasic salt. Both precipitates turn black when dry. (Berzelius.)

F. Arseniate of Lead-oxide with Chloride of Lead.—In many kinds of *Pyromorphite* (p. 149), especially in the yellow variety, the phosphoric acid is partly replaced by arsenic acid. Specific gravity 7·208. (Mohs.) The ore which contains arsenic acid is distinguished from that which contains phosphoric acid only, by the arsenical odour which it evolves when heated on charcoal before the blowpipe, and by being rapidly reduced to metallic lead alloyed with arsenic.

G. Arsenide of Lead and Potassium.—Formed by igniting in a well closed crucible, 2 parts of lead, 1 of arsenious acid, and 2 of tartar. The mass when immersed in water by itself remains almost unaltered,—but if in contact with mercury, which removes the coating of lead, it yields, in the course of a few weeks, a large quantity of arseniuretted hydrogen gas. (Serullus, *J. Phys.* 93, 137.)

Lead and Antimony.

A. Antimonide of Lead.—*a*. $Pb^{15}Sb$.—Found on the hearth of a smelting-furnace at the Mulder works. Broad, thin, six-sided prisms, with two of the lateral faces very much enlarged, and the angles of the lateral edges, about 144°, 97°, and 133°. Specific gravity 9·21. Malleable; of the hardness of calcspar; steel-grey. Fuses less easily than pure lead, and covers the charcoal, first with a white film of lead-oxide, then with a similar film of zinc-oxide, and lastly with a yellow film of lead-oxide. (Karsten, *Pogg.* 55, 118.)

					Karsten.
18Pb	1872	....	93·55	.....	90·10
Sb	129	....	6·45	.....	6·48
Zn		....		.....	1·42
Ca		....		.....	1·50
Ag		....		.....	0·24
Ni, As, S		....		.....	trace
Pb^{18}, Sb	2001	....	100·00	.....	99·74

b. Pb^4Sb.—An alloy of 416 parts lead, and 129 antimony is laminar, brittle, bluish-white, shining, and does not evolve antimony when heated to whiteness in a charcoal crucible. (Fournet.)—*c.* Pb^2Sb.—208 pts. lead with 129 antimony give off but a small quantity of antimony when heated to whiteness in a charcoal crucible.—With 2 At. antimony a larger quantity is evolved, and with 6 atoms, a very large quantity. (Fournet.)

Type-metal contains 83 pts. lead and 17 antimony. (Heeren.) An alloy of 3 pts. lead and 1 pt. antimony is ductile but hard; that which contains equal portions of the two metals is brittle and laminar.

B. Antimoniate of Lead-oxide.—Prepared with nitrate of lead-oxide and antimoniate of potash. Formed likewise by treating antimonide of lead with hot nitric acid.—White curdy precipitate; turns yellow and gives off water when heated; infusible. When ignited on charcoal before the blowpipe, it is reduced, with slight detonation, to antimonide of lead. Not completely décomposed by nitric acid. Insoluble in water. (Berzelius.)

Naples Yellow is antimoniate of lead-oxide. It is formed by mixing intimately 1 part of tartar-emetic, perfectly freed from iron by re-crystallization, with 2 parts of crystallized lead-nitrate and 4 parts of common salt—igniting the mixture in a hessian crucible for two hours, at a heat sufficient to fuse it—separating the cooled mass from the crucible by slight blows—and extracting the chloride of sodium with water. By this treatment, the Naples Yellow is disintegrated and reduced to a fine powder; if too strong a heat has been applied, it forms a hard mass which will not disintegrate.—A cheaper but less beautiful product is obtained by mixing 2 parts of a pulverized alloy of equal parts of lead and antimony (or pulverized printing types) with 3 parts of nitre and 6 of common salt, then heating to redness and exhausting with water as above. (Brunner, *Pogg.* 44, 137; also *J. pr. Chem.* 10, 196.)—Older recipes: 12 pts. white lead, 3 antimonium diaphareticum, 1 sal-ammoniac, 1 alum or pearl-ash; or: 16 grey sulphide of antimony, 24 lead, 1 common salt, 1 sal-ammoniac, &c. The mixture is to be ignited in the air gently at first, but afterwards more strongly for several hours, and then washed.—Orange-yellow, very permanent oil-colour.

C. Sulphantimonite of Lead.—Lead-grey with metallic lustre, easily fusible; when ignited upon charcoal, it evolves sulphurous acid and forms a white and afterwards a yellow deposit. According to Fournet, it leaves antimonide of lead when ignited in the charcoal crucible. Hot nitric acid converts it into a white powder of antimoniate of lead-oxide. Dissolves in strong boiling hydrochloric acid with evolution of sulphuretted hydrogen.—*a. Sexbasic.—Kilkbrickenite.*—Sp. gr. 6·407. (Apjohn, *Jahresber*, 22, 193.)

	Kilkbrickenite.			Apjohn.	Or:			
6Pb	624	....	69·57	.... 68·87	6PbS	720	....	80·27
Sb	129	....	14·38	.... 14·39	SbS^3	177	....	19·73
9S	144	....	16·05	.... 16·36				
Fe		....		.... 0·38				
6PbS, SbS^3	897	....	100·00	.... 100·00		897	....	100·00

b. Quintobasic.—Geocronite.—From Sala: Specific gravity 5·88; massive; light lead-grey (Svanberg, *Pogg.* 51, 535.) From Mevida: Sp. gr. 6·43. (Sauvage, *Jahresber.* 21, 185.)

	Geocronite.			Sauvage.					Svanberg.
5Pb	520	....	66·92	.... 64·89	55Pb	5720	....	69·11	.... 66·45
Sb	129	....	16·60	.... 16·00	6Sb	774	....	9·35	.... 9·58
8S	128	....	16·48	.... 16·90	5As	375	....	4·53	.... 4·70
Cu		....		.... 1·60	88S	1408	....	17·01	.... 16·26
				Zn, 0·11;—Fe, 0·42;—Cu, 1·52;—Bi, Ag, trace					2·05
5PbS, SbS^3	777	....	100·00	.... 99·39		8277	....	100·00	.... 99·04

In the Geocronite from Sala, part of the antimony is replaced by arsenic.

c. Terbasic. — Boulangerite. — Crystallo-laminar or fine-grained. Sp. gr. from 5·69 to 5·97. Dark lead-grey.

	Boulangerite.			Boulanger. Molières.	Thanlow. Lapland.	Bromeis. Nertschinsk.	Abendroth. Oberlahn.
3Pb	312	....	58·10	.... 53·8	.... 55·57	.... 56·29	.... 55·60
Sb	129	....	24·02	.... 25·5	.... 24·60	.... 25·04	.... 25·40
6S	96	....	17·88	.... 18·6	.... 18·86	.... 18·22	.... 19·05
Fe		....		.... 1·2	....		
Cu		....		.... 0·9			
3PbS, SbS^3	537	....	100·00	.... 100·0	.... 99·03	.... 99·55	.... 100·05

d. Bibasic.—Feather-ore.—Soft needles of a lead-grey and smoke-grey colour.

	Feather-ore.				II. Rose.	Or:			
2Pb	208	....	49·88	....	46·87	2PbS	240	....	57·55
Sb	129	....	30·93	....	31·04	SbS^3	177	....	42·45
5S	80	....	19·19	....	19·72				
Fe, 1·30; Zn, 0·08		....		....	1·38				
2PbS, SbS^3	417	....	100·00	....	99·01		417	....	100·00

e. Sesquibasic.—Jamesonite.—Rhombic prisms: $u' : u = 101° 30'$; Sp. gr. 5·56.

	Jamesonite				H. Rose. Cornwall.		Schaffgotsch. Estremadura.
3Pb	312	....	43·70	.....	40·75	.....	39·97
2Sb	258	....	36·13	.....	34·40	.....	32·62
9S	144	....	20·17	.....	22·15	.....	21·79
Bi		....		.....		.....	1·06
Cu		....		.....	0·13	.....	0·42
Fe		....		.....	2·30	.....	3·63
3PbS, 2SbS^3	714	....	100·00	.....	99·73	.....	99·49

f. Four-thirds-basic.—Plagionite.—Crystals belong[illegible] ing to the obliqu[illegible] prismatic system. $u' : u = 120° 49'$. Cleavage paralle[illegible] to u. Sp. gr. 5·4[illegible] Colour dark lead-grey. Decrepitates when heated. ([illegible]inken, *Pogg.* 2[illegible] *492; G. Rose, Pogg.* 28, 421.)

				G. Rose.	Kudernatsch.
		Plagionite		Wolfsberger mine.	
4Pb	416	41·15		40·52	40·98
3Sb	387	38·28		37·94	37·53
13S	208	20·57		21·53	21·49
$4PbS,SbS^3$	1011	100·00		99·99	100·00

Monobasic.—Zinkenite.—Six-sided prisms, probably, as in Arragonite, made up of rhombic prisms. Sp. gr. 5 31. Fracture uneven. Softer than calcspar. Decrepitates strongly before the blowpipe. (G. Rose, *Pogg.* 7, 91.) When ignited in hydrogen gas, it gives off all its sulphur, and leaves a residue of antimony. (Wöhler.)

			H. Rose. Wolfsberger mine.	Or:		
Pb	104	35·02	31·84	PbS	120	40·4
Sb	129	43·43	44·39	SbS^3	77	59·6
4S	64	21·55	22·58			
Cu			0·42			
PbS,SbS^3	297	100·00	99·23		297	100·0

D. Sulphantimoniate of Lead.—When a solution of lead-acetate is gradually added, with constant agitation, to an excess of solution of terbasic sulphantimoniate of sodium, a dark brown precipitate is produced, which, when ignited out of contact of air, gives off sulphur, together with a trace of sulphurous acid, and leaves from 94 to 95 per cent. of residue having the composition of Boulangerite ($3PbS,SbS^3$). Boiling potash-ley extracts the sulphide of antimony from the precipitate and leaves the sulphide of lead; the sulphide of antimony may be precipitated from the filtrate by acids without evolution of sulphuretted hydrogen.—If, on the contrary, the solution of the Schlippe's salt be added by degrees to an excess of lead-acetate, and the mixture boiled for some time, the precipitate will contain a mixture of 8PbS and SbO^5 (compare IV, 358). This mixture, when ignited in close vessels, yields a large quantity of sulphuric acid, a sublimate of antimonic oxide, and a half-fused, lead-grey residue. (Rammelsberg, *Pogg.* 52, 223.)

				Rammelsberg.
3Pb	312	54·83		55·64 to 57·46
Sb	129	22·67		
8S	128	22·50		20·28 to 21·55
$3PbS,SbS^3$	569	100·00		

Lead and Tellurium.

A. Telluride of Lead.—These two metals fuse together with facility. Native telluride of lead is massive; may be cleft parallel to the faces of a cube; has a density of 8·159, and the hardness of calcspar; it may be rubbed to fine powder, and has a yellowish tin-white colour. On charcoal it imparts a blue colour to the blowpipe-flame; in the inner flame it fuses to a bead which gradually diminishes in size till nothing remains but a small globule of silver. This globule is surrounded with an inner ring of telluride of lead which has been volatilized and resolidified, and an outer ring of a brownish-yellow colour, which, when the blowpipe flame is directed upon it, turns blue and then disappears.

(Muschenbroek.) Light lead-grey; close-grained; does not expand in cooling. (Marx.)—*d.* 1 part of lead to 2 bismuth: Fracture crystalline and coarse-grained; does not expand perceptibly in solidifying. (Marx.) —*e.* 1 part lead to 3 bismuth: Fracture laminar; expands slightly in solidifying. (Marx.)—*f.* 1 part lead to 8 bismuth: Coarsely laminar; of the colour of antimony; expands in solidifying. (Marx, *Schw.* 58, 463.) —¶ According to Thomson, the alloy PbBi has a specific gravity of 10·831, and melts at 134·3°; and $PbBi^2$ has a sp. gr. of 10·509, and melts at 128·2°. (Liebig and Kopp's *Jahresber*, 1849, 1040.)—Bi^3Pb^2 fuses at 122·4°. (Person.) ¶

B. Sulphobismuthate of Lead.—$3PbS,BiS^3$.—*Kobellite.*—Specific gravity 6·29...6·32. Fracture radiating. Colour dark lead-grey with metallic lustre, like crude sulphide of antimony; not very hard; yields a black powder. When ignited in an open tube, it yields sulphurous acid and antimonic oxide; fuses with strong intumescence at first, but afterwards quietly, and becomes surrounded with a yellow glass. Forms a white deposit on the charcoal in a weak blowpipe flame, and a yellow deposit in a stronger flame. In the inner flame it fumes strongly and yields a white metallic bead. With carbonate of soda it melts together and sinks into the charcoal, leaving a semi-malleable metallic globule. (Setterberg, *Pogg.* 55, 635.)

					Setterberg. From Nerike.
3PbS	360		57·97		46·36
BiS^3	261		42·03		33·18
FeS					4·72
Cu^2S					1·08
SbS^3					12·70
Matrix					1·45
$3PbS,BiS^3$	621		100·00		99·49

In this mineral, FeS probably replaces part of the PbS, and SbS^3 part of the BiS^3.

Lead and Zinc.

Alloy of Lead and Zinc.—Lead readily unites with zinc, thereby becoming harder; but its ductility is not impaired by any proportion of zinc. (J. F. Gmelin.) When it is heated to whiteness in a charcoal crucible with $\frac{1}{6}$....$\frac{1}{5}$ zinc, the lead gives up the whole of the zinc. (Fournet.)

Lead and Tin.

A. Alloys of Lead and Tin.—Lead and tin unite in all proportions. The alloy is harder, more tenacious and more fusible than either tin or lead alone. From an alloy containing not more than 3 parts of lead to 1 part of tin, vinegar dissolves out nothing but the tin. (Proust, Gummi, Pfaff, *Ann. Chim.* 57, 13; *Schw.* 6, 225; 11, 14.)

The specific gravity of the alloy is below the mean determined by calculation; 2 volumes of tin combine with 1 volume of lead, almost without change of volume (denoted in the table by 2 : 1 M.); but the farther the proportions deviate either way from this standard, the

greater is the difference between the calculated and the actual density, as shown by the following table. In this table the melting points (M.P.) of the alloys are also given.—The specific gravities and melting points of some of the alloys, as determined by Thomson, are likewise added.

	Kupffer.				Thomson.			
	Specific gravity.			M.P.	Specific gravity.			M.P.
	observed.	calculated.	diff.		obs.	cal.	diff.	
Sn^6Pb	7·9210	7·9326	116					
Sn^5Pb	8·0279	8·0372	93	194				
Sn^4Pb	8·1730	8·1826	96	189	7·850	8·545	695	190·0°
Sn^3Pb	8·3914	8·3983	69	186	8·549	9·002	453	182·8
2 : 1M	8·6371	8·6375	4	194				
Sn^2Pb	8·7454	8·7518	64	196	8·688	9·209	521	182·8
SnPb	9·4263	9·4366	103	241	9·288	9·899	611	182·2
$SnPb^2$	10·0782	10·0936	154					
$SnPb^3$	10·3868	10·4122	254	239				
$SnPb^4$	11·5551	10·6002	431					

Regnault (*Ann. Chim. Phys.* 76, 136) found the specific gravity of Sn^2Pb=8·777, and that of SnPb=9·387 at 13·3°.

The alloy Sn^3Pb has one solidifying point, viz. at 187° (182·8 according to Person); the other alloys likewise exhibit a higher solidifying point, which for $Sn^{12}Pb$, is at 210°;—for Sn^6Pb, at 200°;—for Sn^4Pb, at 190;—for Sn^2Pb, at 200°;—for SnPb, at 240°;—for $SnPb^2$, at 270;—and for $SnPb^3$, at 280. (Rudberg.)

32 parts of tin to 1 lead: (*Vierstempliges Zinn*).—5 parts of tin to 1 lead (*Dreistempliges Zinn*). The ordinary proportion fixed by law for tin-vessels.—4 parts tin to 1 lead; *Five-pound Tin* (*Fünfpfündiges Zinn*).—3 parts tin to 1 lead; *Four-pound Tin* (*Vierpfündiges Zinn*). —2 parts tin to 1 lead: *Fine solder; Three-pound Tin* (*Zweistempliges* or *dreipfündiges Zinn*).—1 part tin to 1 lead: *Common solder; Two-pound Tin* (*Zweipfündiges Zinn*).—1 part tin to 2 lead: *Coarse solder.*

B Stannate of Lead-oxide.—An alloy of lead and tin fused in contact with the air oxidizes much more quickly than either metal alone, the change being accelerated by the affinity which the two oxides have for one another. The alloy of 1 part tin with 4 or 5 of lead burns at a red heat like charcoal, the combustion afterwards going on spontaneously like that of inferior peat, with formation of cauliflower-like excrescences. (Berzelius.) The presence of platinum in the alloy retards the combustion; gold, on the contrary, does not interfere with it, being apparently converted at the same time into purple oxide. (Fox, *J. Roy. Inst.* 1, 626.) —Aqueous stannate of potash mixed with a lead-salt gives but a slight precipitate of stannate of lead-oxide: it appears to be somewhat soluble. (Moberg.)—The lead-ash containing tin, or tin-ash containing lead, obtained by oxidating an alloy of the two metals, forms a white opaque *Enamel* when fused either alone or with silica and alkali: *Dial-plates* and other *White Enamels.*

C. Antimonide of Lead and Tin.—Antimonide of tin is rendered brittle by admixture of lead. (Chaudet.)

D. Alloys of Bismuth, Lead, and Tin.—2 parts of bismuth, 1 lead and 1 tin, form Rose's *Fusible metal;* 8 parts bismuth, 5 lead and 3 tin;

Newton's and d'Arcet's; 5 parts bismuth, 2 lead and 3 tin: Lichtenberg's. All these alloys melt below the boiling point of water. An alloy of 426 parts (2 At.) bismuth, 177 (3 At.) tin, and 312 (3 At.) lead, fuses, according to Döbereiner, at 99°.—Rose's fusible metal melts at 93·75°. (G. A. Erman, *Pogg.* 20, 283.)—In whatever proportion the three metals are mixed, they exhibit one fixed solidifying point, at 98°, and two higher ones which are variable. (Rudberg.) — Rose's fusible alloy does not expand in solidifying; hence a glass tube into which the melted alloy is drawn up, cracks lengthwise, when nearly cold. (Marx, *Schw.* 58, 468.)

Sn^4Pb^2Bi has a density of 9·194 at 11°, and fuses at 120°; Sn^2PbBi has a density of 9·253 at 20°, and fuses at 95°. (Regnault, *N. Ann. Chim. Phys.* 1, 137.) $Sn^2Pb^2Bi^3$ fuses at 96°; Sn^2PbBi at 145°. (Person, *Jahresber, L. & K.* 1850, 72.)

120 pounds of an alloy of 3 pts. tin, 2 lead, and 5 bismuth, yielded, on cooling, tolerably definite crystals which fused below 100°, and contained, Sn 15·76,—Pb 26·56,—Bi 57·68, or equal numbers of atoms of the three metals. (Löbell, *J. pr. Chem.* 26, 511.)

Potassium added to fusible metal raises its melting point. (H. Davy.)

E. Alloys of Lead, Tin and Zinc. — The alloy $ZnSn^9Pb^2 = ZnSn^3,2PbSn^3$ exhibits but one solidifying point, viz. at 168°; all other alloys of these three metals have likewise two higher solidifying points, *b* and *c*. (A. & L. Svanberg, *Pogg.* 26, 280.)

Atoms.								Atoms.						
Zn	Sn	Pb		*a.*	*b.*	*c.*		Zn	Sn	Pb		*a.*	*b.*	*c.*
3	11	2	....	168		182	.....	1	12	3	....	168	172	
1	6	1	....	168	171	204	.....	1	18	4	....	168	172	178
1	9	1	....	168	178	183	.....	1	21	6	....	168		175
1	9	2	....	168			.....	1	33	10	....	168		178
1	12	2	....	168		178								

Other Compounds of Lead.

With Iron, Nickel, Copper, Mercury, Silver, Gold, Platinum, Palladium, Rhodium and Iridium.

Chapter XXXII.

IRON.

Bergman. De analysi Ferri. *Opusc.* 3, 1.
Thénard. Oxides of Iron. *Ann. Chim.* 56, 59; also *N. Gehl.* 3, 643.
Bucholz. Oxides of Iron. *N. Gehl.* 3, 696.
Gay-Lussac. Oxides of Iron. *Ann. Chim.* 80, 163; also *Gilb.* 42, 265. Further: *Ann. Chim. Phys.* 1, 33.
Berzelius. Compounds of Iron with Sulphur and Oxygen. *Gilb.* 37, 296; 42, 277. Further: *Ann. Chim. Phys.* 5, 149; also *N. Tr.* 2, 2, 359.—*Pogg.* 7, 393.—Atomic weight of Iron. *Ann. Pharm.* 50, 432.
Rinmann. *History of Iron and its application in the arts and manufactures;* translated into German by Georgi. *Berl.* 1785.
Karsten. *Handbuch der Eisenhüttenkunde.* Halle, 1816.—*System der Metallurgie.* 1831—32. B. 4.

Synonymes. *Eisen, Fer, Ferrum, Mars.*

History. Knives and arms of iron are mentioned in the books of Moses. The ancient Greeks, on account of the difficulty of manufacturing iron, generally used arms made of an alloy of copper and tin.—The chemical relations of iron have been investigated chiefly by Bergman, Proust, Bucholz, Gay-Lussac and Berzelius. Ferric acid was discovered by Fremy.

Sources. The most widely diffused of all the heavy metals. It occurs native, though rarely, sometimes in meteoric masses, sometimes in fine granules in Mica-slate (*Kastn. Arch.* 11, 364), sometimes in Cerite (*Ann. Pharm.* 11, 245); as protoxide; as sesquioxide; as hydrated sesquioxide; as carbonate, phosphate, sulphate, hydrochlorate, silicate, titanate, tantalate, niobiate, pelopiate, tungstate, arseniate, and oxalate of the protoxide or sesquioxide; as protoxide combined with alumina or sesquioxide of chromium; as eight-sevenths sulphide of iron; as bisulphide; as sulphide of iron combined with other metallic sulphides, in Copper pyrites, Peacock copper, Grey copper, Arsenical pyrites, and Sternbergite; and finally, in small quantity, often as a colouring principle of various tints, in a great number of mineral substances; and in most organic bodies.

Preparation on the large scale.—Principally from ores containing the protoxide or sesquioxide. The ores are commonly roasted in the first instance to free them from sulphur, arsenic, &c., then coarsely pounded, mixed with charcoal or coke, and a flux to facilitate the fusion of the earthy

matters contained in the ore, and exposed to the most intense white heat in tall smelting furnaces (*Hoheisenöfen*) urged by a strong blast. If the ore contains alumina and silica, lime is used as a flux; a calcareous ore, on the contrary, requires the addition of minerals containing silica and alumina: the best mode of proceeding is to mix calcareous with siliceous iron-ores, so that each may act as a flux to the other.—The iron reduced from the melting mass—*Pig-iron, Cast-iron*—which is freed from time to time from the slag which floats on its surface, and run off at the bottom, or scooped out several times in a day—is contaminated with various matters which will be mentioned under the head of *Cast-iron:* from these it is freed on the large scale by a partial oxidation, called the *Refining process* (*das Eisenfrischen oder Frischprocess*), whereby chiefly the foreign substances are oxidized, and separated partly as gas, partly in the form of a slag, called *Cinder* (*Frischschlacke*), whilst a purer and malleable iron remains, called *Refined iron, Bar iron,* or *Wrought iron* (*Frischeisen, Stabeisen, Schmiedeisen*). The carbon which is oxidized, partly by the air, and partly by the cinder produced in the process, escapes in the form of carbonic oxide; the cinder consists of silicate of lime, magnesia, alumina, manganous oxide, ferrous oxide, &c. In proportion as the iron becomes purer, it loses its liquid form and becomes granular: as the purification advances, it welds together, and is then perfectly purified and formed into bars either under the hammer or between rollers. This oxidation takes place either by fusion with charcoal while a blast of air is blown upon the mass: *Refining upon hearths* (*Frischbarkeit auf Heerden*), or by contact with the flame of coal in reverberatory furnaces: *Puddling.*

Bar-iron still retains about ½ per cent. of carbon, which makes it harder; generally also it contains a small quantity of silicium; sometimes phosphorus, which makes it brittle when cold;—or sulphur, arsenic, copper, which make it brittle at a red heat,—and other metals.

Purification.—1. By melting iron filings with one-fourth their weight of smithy scales under a layer of green glass,—or of glass prepared for the purpose and free from heavy metals—the whole being enclosed in a crucible with the cover luted down, and the fire urged by a strong blast. (Broling.) By reducing a pure oxide of iron with hydrogen gas. (Berzelius.)

Properties. Iron sometimes exhibits cleavage parallel to the faces of a cube. This was observed by Wöhler (*Pogg.* 26, 182) in iron-plates which had been imbedded beneath the hearth of an iron-smelting furnace and exposed to a strong white heat during the whole time of smelting. The same appearance was noticed by Breithaupt (*J. pr. Chem.* 4, 245) in the Aachner meteoric iron. Wöhler likewise found iron crystallized in octohedrons in the hollows of a large cast-iron roller.—Wrought iron has a fibrous texture. It is the hardest and toughest of all the ductile metals; it cannot be beaten out into very thin plates, but may be drawn out into very fine wire. Iron purified (1) by fusion with smithy-scales has, after solidification, a density of 7·8439, which is rather increased than diminished by rolling out into plates or drawing into wires. (Broling.) The purest soft bar-iron, containing but a trace of carbon, has a density of 7·79 (Karsten); that of ordinary bar-iron is 7·788. (Brisson.)—At a red heat, iron becomes softer and tougher; at a white heat, it may be welded; at a temperature above the welding point, it crumbles under the hammer; its melting point approaches the limits

of temperature that can be obtained by ordinary means,—being, according to Pouillet, at 1550° C., according to Daniell, at 1587°, according to Morveau, at 6346° C. or 175° Wedg., and according to Mackenzie, at 158° Wedg. At a still higher temperature, such as that produced by Hare's deflagrator, or by the combustion of iron in oxygen gas, it volatilizes. If an electric current be passed by means of charcoal points through iron placed in vacuo, there is formed a quantity of vapour of iron, which burns with a flash on admitting the air, and deposits a yellowish-red film upon the glass. (Hare.)—Iron is attracted by the magnet, and may itself be rendered magnetic, but loses this property the more quickly in proportion as it is free from carbon. Iron reduced from the oxide by hydrogen is a grey powder (Berzelius); in this state it does not conduct electricity. (Higgins & Draper, *N. Edinb. Phil. J.* 14, 315.)

Atomic weight of Iron=27·137 (Berzelius)=25·68 (Capitaine, *Ann. Chim. Phys.* 77, 126.)—¶ According to a more recent determination of Berzelius (*Ann. Pharm.* 50, 432), the true atomic weight of iron is 28. The errors in previous determinations appear to have arisen from the neglect of making due allowance for the impurities contained in the iron. ¶

Compounds of Iron.

Iron and Oxygen.

1. Iron when in solid masses remains unchanged in the air at ordinary temperatures; the finely divided iron obtained by decomposing the sesquioxide by hydrogen gas at as low a temperature as possible—if allowed to cool perfectly in the atmosphere of hydrogen and then exposed to the air — instantly takes fire and is converted into sesquioxide. (Magnus, *Pogg.* 3, 81; 6, 509; *comp.* II. 27; and Stromeyer, *Pogg.* 6, 471.) Iron reduced by hydrogen at a red heat, does not take fire till heated nearly to redness.

2. Coherent iron heated to redness in the air oxidizes without visible combustion, and forms ferroso-ferric oxide: *Scale-oxide of Iron, Smithy-scales*—which, by prolonged ignition, is converted into ferric oxide (sesquioxide). The successive shades of yellow, red, blue, and lastly grey, with which polished iron becomes covered during the operation of tempering, are due to the very thin films of ferroso-ferric oxide, which transmit light more or less, producing the tints of Newton's coloured rings.

3. Iron heated to whiteness in the air or in oxygen gas burns with vivid sparkling, and forms ferroso-ferric oxide; in common air, the combustion soon ceases; but in oxygen gas it continues, if the piece of iron be thin (*comp.* II. 34); and the high temperature thereby produced, causes the volatilization of part of the iron, which is then converted into sesquioxide. A bar of iron heated till it emits sparks (*i. e.* to the welding point) will burn even in the air, if the blast of the bellows be strongly directed upon it, or if it be swung rapidly round. (Addams, *Phil. Mag. J.* 11, 407, and 446; also *J. pr. Chem.* 12, 317; Boerley, Stratingh, *N. Br. Arch.* 22, 305; Darcet, *Pogg.* 31, 496.) In the collision of flint and steel, fine particles of steel are detached by rubbing on the stone, and brought to such a temperature that they take fire in the air, and impart their combustion to tinder. Hence, according to H. Davy (*Gilb.* 17, 446),

a flint and steel in vacuo gives but very faint sparks, proceeding from ignited particles of stone; and, according to the same authority, iron in very fine particles takes fire much below a red heat.

4. Iron when covered with a thin layer of water and exposed to the air, is converted into hydrated sesquioxide, by taking up the oxygen which the water absorbs from the air, and combining as oxide with a portion of the water. In this reaction, there is likewise produced a portion of ammonia, which partly escapes and partly remains in combination with the hydrated ferric oxide;—the formation of the ammonia is due to the decomposition of a portion of the water, and to the combination of its hydrogen with the nitrogen of the air which has been absorbed by the water. (II. 418, 419.) If the iron be covered by a deeper stratum of water in a vessel exposed to the air, so that the transference of the oxygen of the air through the water to the iron may take place more slowly, a formation of black hydrated ferroso-ferric oxide takes place, because hydrated ferric oxide, as it slowly forms, induces the iron to decompose the water, and form ferrous oxide, with which the ferric oxide then unites. (Wöhler.)—Iron remains unaltered in damp air, provided no water is deposited upon it—as, for example, under a bell-jar, closed at bottom with a water-joint, and having a piece of tarnished lead likewise placed under it, the water being then deposited exclusively upon the lead. But if there are cracks in the iron, and these cracks are filled with scale-oxide, water becomes deposited upon this oxide, and rusting then takes place. Iron also rusts quickly in damp air containing small quantities of sulphuretted hydrogen (which first forms sulphide of iron and then ferrous sulphate), chlorine, hydrochloric acid, and acetic acid; but carbonic acid and ammonia have no influence. (Bonsdorff, *Pogg.* 42, 332.)—Iron does not rust in the air under water containing small quantities of alkaline substances. When immersed in aqueous ammonia, potash, or soda, it remains bright for months. If water at 22° be saturated with hydrate of potash, one measure of this solution is sufficient to impart this preservative power to 2000 measures of water; but if the mixture contains from 4000 to 5000 measures of water, iron rusts when immersed in it; it likewise rusts in a mixture containing from 1000 to 2000 measures of water, if the liquid be completely saturated with carbonic acid. One measure of a saturated solution of carbonate of soda may be diluted with 54 measures of water without causing iron to rust; but if the quantity of water be increased to 59 measures, iron rusts when immersed in it. One measure of a saturated solution of borax may be diluted with 6 measures of water, and one measure of lime-water with three measures of water, without losing its preserving power; but if the proportion of water be increased in either case, rusting ensues. The preserving influence of alkalis does not, in all probability, arise from their power of withdrawing carbonic acid from the water; for iron rusts even under thoroughly boiled water, in contact with air free from carbonic acid; it is true that the mixture of aerated water with potash has the effect of expelling the air; but if the water is in great excess, the expulsion is very imperfect: moreover, carbonate of soda drives out but a small quantity of air, and borax none; and yet these substances prevent oxidation. (Payen, *Ann. Chim. Phys.* 50, 305.)—Wetzlar (*Schw.* 49, 484) showed, long before Payen, that iron does not rust in aqueous solution of potash or ammonia, even though the solution may be diluted, and that in saturated solutions of sulphate or nitrate of potash, it oxidates more slowly than in pure water, inasmuch as, according to his observations, these liquids contain less air in solution.

Hall (*N. Quart. J. of Sc.* 3, 262; also *Pogg.* 14, 145) likewise found that iron does not rust under water into which lime or magnesia has been thrown, or even in a mixture of 1 part of lime-water with 4 parts of water.—Iron rusts more slowly in proportion as its surface is smoother; the rust is formed most abundantly in cracks. The purest iron rusts the most quickly; hard wrought iron, richer in carbon, rusts more slowly; then follows soft steel, then hard steel, then soft cast-iron, and lastly hard cast-iron. The presence of sulphur in iron accelerates the rusting; phosphorus appears to retard it. Beneath the flocculent hydrated sesquioxide, there is formed a thin black crust [of ferroso-ferric oxide?] which adheres firmly to the iron. Contact with zinc protects the iron from rusting only so long as the zinc does not itself become covered with a film of oxide. Tin in contact with iron accelerates the rusting. (Mor. Meyer, *J. techn. Chem.* 10, 833.)—A water-conduit consisting of cast-iron pipes became stopped up in the course of a few years by the formation of tuberculous masses of hydrated ferric oxide. According to Payen, grey cast-iron oxidates more readily than white, and even than bar-iron; in iron pipes, grey and white cast-iron are mixed: now, if the water contains too little alkali to protect the iron completely, the parts consisting of grey iron become oxidated and produce the formations of rust. When cast-iron of this description is exposed to the action of a mixture of 75 measures of aerated water, and one measure of a saturated solution of common salt and carbonate of soda, oxidation begins in a minute, and there is formed,—first, whitish hydrated ferrous oxide and hydrated ferroso-ferric oxide, which at some distance from the iron, are converted into hydrated ferric oxide,—and afterwards carbonate and silicate of ferrous oxide, the latter being produced by the oxidation of silicide of iron. In water containing nothing but common salt, protochloride of iron is likewise formed. In water containing 0·2 per cent. of soda-hydrate and 0·6 of common salt, the oxidation is confined within smaller spaces around the points at which it originates, and spreads in vermicular forms. At the oxidized points, the iron becomes richer in graphite, and at the same time blacker and softer. (Payen, *Ann. Chim. Phys.* 63, 405.) Since this rapid rusting seldom takes place in cast-iron water-pipes, it is probable that a peculiar composition of the cast-iron is necessary to its occurrence. (Gm.)

5. Red-hot iron in contact with aqueous vapour liberates hydrogen, and is converted into ferroso-ferric oxide FeO,Fe^2O^3, in small octohedrons. (Gay-Lussac, Despretz, *Ann. Chim. Phys.* 62, 346.) According to Haldat (*Ann.Chim. Phys.* 46, 70), rhombohedrons of ferric oxide are formed, similar to those of specular iron; but they were not analyzed.—According to Stromeyer (*Pogg.* 9, 475), the iron takes up variable quantities of oxygen, the amount being greater as the temperature is higher and the action of the aqueous vapour more prolonged. According to Bucholz, ferrous oxide is produced.

6. At ordinary temperatures, and out of contact of air, iron does not decompose thoroughly boiled water, unless it is in contact with more electro-negative bodies, as with previously formed ferric oxide, mercury, &c.: in this case, and likewise when the liquid is heated to 50° or 60°, a feeble evolution of hydrogen takes place, and ferroso-ferric oxide appears to be formed. (Hall, *Quart. J. of Sc.* 7. 55; Guibourt, *Ann. Chim. Phys.* 11, 43; also *J. Pharm.* 4, 241.)

7. In presence of acids which do not themselves give up oxygen, iron quickly decomposes water, and is converted, with evolution of hydrogen,

into ferrous oxide, which combines with the acid. The evolution of hydrogen takes place even in aqueous carbonic acid; but it ceases on the addition of lime.

8. By heated oil of vitriol, by nitric acid, hypochlorous acid, and other acids, which retain their oxygen less forcibly—also by hypochlorites, and, at a red heat, by nitrates, chlorates, nitrous gas, &c., iron is converted, at the expense of the acid, into ferric oxide. When iron filings are gently heated with fuming nitric acid, explosion takes place.

[For the behaviour of iron with anhydrous sulphuric acid at a red heat, see II. 178.]

A. *Sub-oxide of Iron?*

When iron is burnt in the flame of the oxy-hydrogen blowpipe, the product of the combustion is not scale-oxide of iron, as when the metal is burnt in oxygen gas, but a fused and somewhat malleable mass, which dissolves in hydrochloric acid with evolution of hydrogen, forming a solution of ferrous hydrochlorate, and invariably contains 6·79 per cent. of oxygen; it is therefore Fe^4O or Fe^3,FeO. (Marchand, *J. pr. Chem.* 18, 184.)

B. Ferrous-oxide. FeO.

Protoxide of Iron, Eisenoxydul, Oxyde-ferreux.

Formed in the solution of iron in such aqueous acids as do not easily give up their oxygen.

Not known in the separate state.

			Lavoisier, Proust.	Döbereiner.	Bucholz.	Berzelius. earlier.	Berzelius. later.	Gay-Lussac.
Fe	27	77·143	73	76·9	77	77·22	77·62	77·94
O	8	22·857	27	23·1	23	22·78	22·38	22·06
FeO	35	100·000	100	100·0	100	100·00	100·00	100·00

(FeO = 339·21 + 100 = 439·21. Berzelius.)

Combinations. *a.* With Water.—Hydrate of Ferrous Oxide or Ferrous Hydrate.—Thénard's statement that this substance is a peculiar white oxide of a lower degree of oxidation, has been disproved by Proust, Bucholz, and more especially by Berzelius. (*Schw.* 22, 334.)—The hydrate is precipitated on mixing a solution of a ferrous salt, perfectly free from ferric oxide, with solution of potash perfectly freed from air by boiling, the precipitation being performed in a vessel from which the air is excluded. The white flakes which fall must be carefully preserved from contact of air during washing and drying. The vessel in which the precipitation by potash is performed must be immediately filled up with thoroughly boiled water and then closed. As soon as the precipitate has settled down, the liquid is decanted with a siphon, leaving only a thin layer above the precipitate; the vessel again filled with boiling water poured in very slowly so as not to disturb the precipitate; and afterwards shaken and closed. This purification by alternate subsidence and decantation must be performed as quickly as possible, because ferrous oxide decomposes water by continued contact, and is converted into

ferroso-ferric oxide. The light green precipitate is then introduced as quickly as possible into a tubulated retort, having its neck fitted with a stop-cock from which proceeds a tube 28 inches long, bent downwards, and dipping into mercury; ether is poured upon it; the tubulature closed, heat applied till the ether vapour, together with the air of the retort, has all escaped through the mercury; and the retort afterwards kept warm and the tube cool—so that the water may distil off and condense in the tube—till the precipitate is quite dry. The stopcock is then closed, and the whole left to cool; after which the retort is filled with hydrogen gas, and its contents emptied as quickly as possible, under a bell-jar filled with hydrogen gas, into small, wide-mouthed, well-stopped bottles. If a ferrous salt be precipitated by excess of ammonia instead of potash, the precipitate, after long standing, gives off hydrogen gas, becomes gradually darker in colour, and when dried in the manner above described, is converted into black ferroso-ferric oxide containing ammonia. (G. Schmidt, *Ann. Pharm.* 36, 101.)

Dried ferrous hydrate is a brittle, easily friable mass, of a fine green colour. (G. Schmidt.) The green colour is probably due to incipient oxidation. It is not magnetic. (Wöhler & Liebig.) On exposure to the air, it is instantly converted into ferric oxide, the change being attended with an evolution of heat which often rises to redness. It absorbs carbonic acid gas with violence, becoming at the same time hot and black, and dissolves in aqueous acids with great development of heat. (G. Schmidt.) When the liquid in which the white flakes of hydrated ferrous oxide have been precipitated is heated to ebullition, they turn black, in consequence (according to Wöhler & Liebig) of the formation of hydrated ferroso-ferric oxide by the action of the air. The protoxide, if exposed to the air while still moist, quickly changes to dingy green hydrate of ferroso-ferric oxide, and afterwards to yellowish-brown hydrate of ferric oxide.

b. With Acids, forming the Salts of Ferrous-oxide, or Ferrous Salts. *Proto-salts of Iron.*—The affinity of ferrous oxide for acids is considerable. Ferrous salts are, for the most part, white when anhydrous, and pale greenish-blue in the hydrated state. The soluble salts have at first a sweetish, and afterwards an inky taste. They give off their acid on ignition if the acid is volatile. The residue obtained by igniting a ferrous salt out of contact of air, consists of ferric oxide, if the acid—such as sulphuric or nitric acid—gives up its oxygen readily; of ferroso-ferric oxide, if the acid, *e. g.*, carbonic acid, retains its oxygen more forcibly; and of metallic iron if the acid is organic. Before the blowpipe, with carbonate of soda, borax and microcosmic salt, ferrous salts exhibit the reactions of ferric oxide. They extract oxygen from the air and from various oxidized compounds—viz., from water in presence of chlorine, from hypochlorous acid, from nitric acid, and from the oxides of silver, gold, and palladium dissolved in acids—and are thereby converted into ferric salts. If no excess of acid is present to hold in solution the whole of the ferric oxide thus produced, part of it is precipitated in the form of a yellowish-brown basic salt. When nitric acid is the oxidizing agent, so long as any portion of ferrous salt remains unconverted into ferric salt, the nitric oxide separated from the nitric acid does not escape from the liquid, but is absorbed by the excess of ferrous salt and forms a dark greenish-brown solution. A concentrated solution of sulphate or hydrochlorate of ferrous oxide placed in the circuit of a hundred-pair voltaic battery, deposits

metallic iron in small granules on the negative platinum wire. If the positive wire is dipped into a solution of common salt separated from the iron-solution by moist clay, the iron is obtained in glittering crystals which exhibit magnetic polarity. (Becquerel.) Zinc immersed in a perfectly neutral solution of ferrous sulphate or hydrochlorate contained in a stoppered bottle, throws down metallic iron (together with oxide) which is deposited partly on the zinc, partly on the contiguous side of the glass. (Fischer, *Pogg.* 9, 266.) If plates of zinc and copper soldered together are immersed in the perfectly neutral hydrochlorate solution, the iron is deposited on the copper in the form of a bluish-white, metallic, very friable mass, which, when gently ignited in hydrogen gas, becomes very tough. (Capitaine, *N. Ann. Chim. Phys.* 2, 126.) Anthon (*Repert.* 77, 121) obtained with zinc, not metallic iron, but light green flakes of ferroso-ferric oxide which gradually acquired a darker colour. [Was the air perfectly excluded?]—Hydrosulphuric acid precipitates only those ferrous salts which contain a weaker acid; *e. g.*, the aqueous acid carbonate, and the neutral oxalate, tartrate, and acetate, the precipitation in the three last-mentioned salts, going on only till a moderate portion of acid is set free (Gay-Lussac); the same re-agent precipitates the benzoate of ferrous oxide, and even, to a slight extent, the sulphate and hydrochlorate, if the acids are completely saturated with base. (Grischow, *Schw.* 27, 185.) The same result was obtained by Wackenroder (*N. Br. Arch.* 16, 118), who states that hydrosulphuric acid throws down a large quantity of iron from acetate of ferrous oxide, or from the sulphate or hydrochlorate mixed with acetate of potash; but not the whole of it, even when the acetate of soda is in excess. The black precipitate is hydrated protosulphide of iron, which acquires a rusty brown colour by exposure to the air. It dissolves readily in hydrochloric or sulphuric acid, and likewise in a large quantity of acetic acid, provided it does not contain excess of sulphur. (Wackenroder.) The corresponding precipitates of cobalt and nickel oxidate much more slowly by exposure to the air.—The same precipitate, but containing the whole of the iron, is produced in all ferrous salts on the addition of an alkaline hydrosulphate; and it is not soluble in an excess of the re-agent. Hydrosulphate of ammonia dissolves a mere trace of it, but gives it up again on exposure to the air, or on the addition of hydrosulphite of ammonia. (Wackenroder.) A very dilute iron-solution to which hydrosulphate of ammonia is added, assumes a green colour, from the presence of iron in a state of suspension.—Fixed caustic alkalis completely precipitate the iron in the form of a white hydrate, which, by exposure to the air, acquires a dingy green and afterwards a red-brown colour.—Ammonia throws down part of the iron in the form of hydrate, the rest remaining dissolved in the liquid, which, when exposed to the air, becomes covered first with a green and afterwards with a brown film. If the ferrous salt is previously mixed with sal-ammoniac, ammonia yields no precipitate, but forms a pale green mixture which exhibits similar appearances on exposure to the air.—Monocarbonate of potash or soda and sesquicarbonate of ammonia throw down white carbonate of ferrous oxide, which soon acquires a green and afterwards a brown colour by exposure to the air—and if sal-ammoniac be added, dissolves in the liquid, which then exhibits a green and subsequently a brown turbidity on exposure to the air. Bicarbonate of potash or soda forms the same precipitate, with evolution of carbonic acid; but if the solutions are dilute, a clear mixture is formed, which deposits ferrous carbonate on boiling, and on exposure to the air,

elds a precipitate of hydrated ferroso-ferric oxide.—Carbonate of lime oes not precipitate ferrous salts. (Fuchs.)—Phosphate of soda precipitates (up to a thousand-fold dilution: *Pfaff*) white phosphate of ferrous xide, which acquires a bluish-green colour by exposure to the air. Arseniate of soda precipitates (up to a thousand-fold dilution: *Pfaff*) white arseniate of ferrous oxide, which becomes dingy-green on exposure to the air.—Oxalic acid and acid oxalate of potash communicate a yellow colour to ferrous salts, and, after a while, throw down yellow oxalate of ferrous oxide, the precipitation being immediate when an alkaline oxalate is used.—Ferrocyanide of potassium forms a precipitate which is white, if the solution has been perfectly freed from air by boiling and the iron-salt is absolutely free from ferric oxide, but otherwise bluish-white: by exposure to the air, this precipitate is converted into Prussian-blue. Ferricyanide of potassium gives a precipitate of Prussian-blue even in very dilute solutions.—Tincture of galls neither colours nor precipitates ferrous salts, when they are quite free from ferric oxide; but the mixture acquires a violet-black colour on exposure to the air. According to Pfaff, tincture of galls gives a purple colour and precipitate with aqueous acid carbonate of ferrous oxide.

Those ferrous salts which are insoluble in water, dissolve in aqueous hydrochloric acid. Both the aqueous and the hydrochloric acid solutions absorb large quantities of nitrous gas, thereby acquiring a dark brown colour. (Vid. *Sulphate* and *Hydrochlorate of Ferrous-oxide.*)

C. Ferroso-ferric Oxide.

Eisenoxydoxydul, Deutoxyde de Fer.—The name *Ferroso-ferric oxide* is applied to oxides of iron which contain more oxygen than the protoxide and less than the sesquioxide, and may be regarded as compounds of the protoxide and sesquioxide in various proportions.

a. Scale-oxide.—$6FeO, Fe^2O^3$. When iron is heated to redness in the air, two layers of scale-oxide are formed, which may easily be separated. The inner layer, $6FeO, Fe^2O^3$, is blackish-grey, porous, brittle, and attracted by the magnet. The outer layer contains a larger quantity of ferric oxide, but in variable proportion; it is of a reddish iron-black colour, dense, brittle, yields a black powder, and is more strongly attracted by the magnet than the inner layer. The amount of ferric oxide in the outer layer is between 32 and 37 per cent., and on the very surface it is as much as 52·8 per cent. (Mosander, *Pogg.* 6, 35; also *Schw.* 47, 81.) Specific gravity of the scale-oxide=5·48. (P. Boullay.)

				Or:				Mosander.	Berthier.
8Fe	216	....	75	6FeO	210	....	72·92	.... 72·56	.... 64·2
9O	17	....	25	Fe^2O^3	78	....	27·08	.... 26·41	.... 35·8
				Silica		....		.... 1·03	....
$6FeO,Fe^2O^3$	288	....	100		288	....	100·00	.... 100·00	.... 100·0

Berthier (*Ann. Chim. Phys.* 27, 19; also *Schw.* 43, 319) regards th scale-oxide as $4FeO, Fe^2O^3$; Mosander attributes the greater amount o ferric oxide found by Berthier to the fact of Berthier having analyzed th inner and outer layers together.

b. Magnetic Oxide. FeO, Fe^2O^3.—Found native; likewise in ma meteorites.—*Formation.* 1. In the rapid combustion of iron, either oxygen gas or in the air. (Mitscherlich, *Pogg.* 15, 632.)—2. By ignit

iron (or the scale-oxide: *Regnault*) in an atmosphere of hydrogen gas. (Gay-Lussac, Despretz.) The iron plates which are laid beneath the hearths of iron-smelting furnaces and are exposed to a red heat, are, in the course of 6 or 10 years, completely converted by the moisture of the soil into magnetic oxide, partly crystalline, partly amorphous and attracted by the magnet (but not itself magnetic). The same compound is formed on the under side of the refining hearths, where the iron comes in contact with aqueous vapour. (Koch, *Ueber Krystall. Hüttenproducte*, s. 17.)—By fusing protochloride of iron at a low red heat with dry carbonate of soda and extracting the chloride of sodium with water, the magnetic oxide is obtained in the form of a black heavy powder. (Liebig & Wöhler, *Pogg.* 21, 582.) [Is the higher oxidation of the iron in this process due to the oxygen of the air or to the carbonic acid of the carbonate of soda ?]

The native oxide crystallizes in forms belonging to the regular system; *Fig.* 2, 3, 5, 6, &c. Cleavage indistinct, parallel to *o*. Harder than fluor-spar; sp. gr. 5·094. Fracture conchoidal. Colour iron-black; yields a black powder. Fuses more readily than iron; with difficulty before the blowpipe. Attracted by the magnet and often itself magnetic. The oxide prepared by (2) has a specific gravity of 5·40. Crystallizes in the forms represented in figures 1, 4, and 8. (Koch.)

			Berzelius. Narra.	Fuchs. *native.*	Despretz. *prepared by* (2)	Gay-Lussac.
3Fe	81	71·68	71·86	71·91	72·46	72·5
4O	32	28·32	28·14	28·09	27·54	27·5
Fe^3O^4	113	100·00	100·00	100·00	100·00	100·0

			Berzelius. Narra.	Fuchs. *native.*	Despretz. Brazil.	Gay-Lussac. Schwarzenstein.
FeO	35	30·97	31	30·88	20	25
Fe^2O^3	78	69·03	69	68·40	72	75
FeO,Fe^2O^3	113	100·00	100	99·28	100	100

(Fe^3O^4 = 3 . 339·21 + 400 = 1417·63. Berzelius.)

The analysis of the magnetic oxide from Schwarzenstein corresponds to the formula $3FeO,4Fe^2O^3$, probably because the ore contains specular iron mixed with it. (Von Kobell, *Schw.* 62, 195; 64, 429; *J. pr. Chem.* 1, 86.) [For Karsten's analyses of various kinds of magnetic iron-ore *vid. Karsten's Arch. f. Bergb. u. Hüttenk.* 16, 17.]—On the hearths of puddling furnaces there is formed a mixture of ferrous silicate and magnetic oxide; the latter is found crystallized in geodes of regular tetrahedrons, truncated octohedrons, and rhomboidal dodecahedrons; these crystals dissolve in hydrochloric acid, with separation of gelatinous silica, and contain 35 per cent. of ferrous oxide, 58 p. c. of ferric oxide, and 7 of silica. (Laurent & Holms, *Ann. Chim. Phys.* 60, 330; also *J. pr. Chem.* 7, 339.) Probably a mixture of $3(FeO,Fe^2O^3)$ and FeO,SiO^2.

Decompositions of Ferroso-ferric Oxide.—Reduced to the metallic state by charcoal at a white heat. Pounded scale-oxide ignited in a charcoal crucible is converted on the outside into soft pulverulent metallic iron of a blackish-blue colour; further inwards is found olive-green iron which is very pure, and free from carbon and oxygen; and finally in the middle there is formed a mixture of olive-green iron and undecomposed scale-oxide; no free protoxide is found in any part of the mixture.—2. To

the metallic state by hydrogen gas at all temperatures between 400° and the strongest heat of the wind-furnace; generally, at the same temperature as water, on the other hand, is decomposed by metallic iron. (Gay-Lussac; *comp.* I. 125.)—Ammoniacal gas likewise reduces the iron at a red-heat. —*Ferrum pulveratum* might perhaps be best prepared by reducing scale-oxide with hydrogen gas in an iron tube.—3. Carbonic oxide gas acts like hydrogen; it reduces red-hot ferroso-ferric oxide to the metallic state, with formation of carbonic acid, and, on the other hand, carbonic acid is reduced by iron to the state of carbonic oxide, with formation of ferroso-ferric oxide. (Despretz, *Ann. Chim. Phys.* 43, 222; also *Pogg.* 18, 159; Göbel, *J. pr. Chem.* 6, 386; Leplay & Laurent, *Ann. Chim. Phys.* 65, 404.)—Carbonic acid gas mixed with an equal volume of carbonic oxide likewise converts red-hot iron into ferroso-ferric oxide. (Laurent, *Ann. Chim. Phys.* 65, 423.)—4. Potassium and sodium at about 300° likewise reduce ferroso-ferric oxide to the metallic state, the reduction being attended with a slight evolution of light and heat.—5. By ignition with sulphur, this oxide yields sulphurous acid and sulphide of iron.—6. When finely pulverized and treated with a quantity of dilute hydrochloric acid, less than sufficient to dissolve it completely, it is resolved into ferrous oxide which dissolves, and red ferric oxide which remains undissolved. (Berzelius, *Schw.* 15, 291.)

Combinations.—*a.* With Water.—Hydrate of Ferroso-ferric Oxide.—*α. Dingy-green Hydrate.*—By exposing the white hydrate of ferrous oxide to the air for a short time,—or by precipitating a mixture of a ferrous salt and a small quantity of ferric salt with potash or ammonia—a dingy green hydrate of ferroso-ferric oxide is obtained, which, on further exposure to the air, is quickly converted into rusty brown hydrate of ferric oxide.

β. Black Hydrate.—Precipitated from a solution of magnetic oxide in hydrochloric acid, or from a mixture of ferrous and ferric salts containing 1 At. FeO to 1 At. Fe^2O^3, on the addition of potash or ammonia. The yellow solution of magnetic oxide in hydrochloric acid yields with ammonia a brownish-black precipitate which is magnetic even while in the liquid, so that it collects round a magnet dipped into that liquid. It may be washed on the filter without becoming more highly oxidized. (Liebig & Wöhler, *Pogg.* 21, 583; also *Mag. Pharm.* 34, 138.)—2. The same precipitate is obtained by mixing sulphate of ferric oxide and ammonia with sulphate of ferrous oxide, in such proportion that the ferric oxide present in the mixture may contain three times as much oxygen as the ferrous oxide, and precipitating with ammonia. If the quantity of ferrous sulphate is greater than the above, the precipitate will contain an excess of hydrated ferrous oxide, which will oxidate more quickly; if, on the contrary, the ferric salt is in excess, the precipitate will contain free hydrated ferric oxide, from which the hydrated ferroso-ferric oxide may be separated by the magnet. (Abich, *Pogg.* 23, 354.)—3. Two equal portions of ferrous sulphate are taken; the first is dissolved in water acidulated with sulphuric acid, and oxidated at a boiling heat by the addition of nitric acid in small portions at a time. The other portion is dissolved in water freed from air by boiling. The two solutions are then mixed; the mixture, while still hot, precipitated by ammonia added at once in excess; and the liquid, together with the brown-black precipitate, heated for some minutes to the boiling point. The precipitated ferroso-ferric oxide is then collected on a filter and washed—during

which process it undergoes further oxidation—and then dried at a gentle heat. (Wöhler, *Ann. Pharm.* 22, 56.) [This process should yield $2FeO,Fe^2O^3$; but even if a greater quantity of ferric oxide is not produced by the nitric acid still remaining, or by contact with the air, the proportion of that oxide is sure to be increased by decomposition of water.]—Mercer (*Phil. Mag. J.* 20, 340) adopts the same process, excepting that he boils the liquid down so as to expel any accidental excess of nitric acid and precipitates by potash at a boiling heat instead of by ammonia. The precipitate when examined by the microscope appears to consist of brown transparent laminæ.—4. Böttger (*Beitrage*, 2, 12) precipitates ferrous sulphate free from ferric oxide by the addition of carbonate of soda; washes the precipitate several times by decantation; and then boils it with tolerably concentrated caustic potash. This process yields a velvet-black powder, much less liable to absorb an additional quantity of oxygen than that which has been precipitated by ammonia. [No hydrogen is evolved on boiling the precipitate with potash out of contact of air, and the precipitate remains greyish-white. Gm.]—5. Noel (*N. J. Pharm.* 1, 62) precipitates ferrous sulphate with carbonate of soda, washes the ferrous carbonate by decantation, leaves it to drain upon linen, and then heats it in a cast-iron vessel, with constant stirring, till it is dry. It is thereby converted into a velvet-black powder. Soubeiran obtained by this process a precipitate which was not perfectly black, and when treated with hydrochloric acid, evolved carbonic acid.—6. Preuss introduces 4 parts of pulverized iron and 5 parts of ferric oxide into a flask, together with a two or threefold quantity of water, and boils the liquid gently for some time. The mixture gives off fetid hydrogen gas and turns dark brown at first, but afterwards black. When the evolution of gas ceases and the resulting black powder settles down readily, it is separated by levigation from the excess of iron; thrown on a filter of grey porous paper; and the filter, after the water has drained off, is wrapped up in a large quantity of paper, and quickly dried in hot air.—The black, very loose powder dissolves in acids without evolution of gas, and the solution yields a black precipitate on the addition of an alkali. The precipitate must not be dried by heat, because in that case it would turn brown from higher oxidation. In the formation of ferroso-ferric oxide by this process, the ferric oxide does not give up oxygen to the iron, but induces the decomposition of the water, by its predisposing affinity for ferrous oxide. Zinc is not oxidated by boiling with water and hydrated ferric oxide; the hydrates of alumina and chromic oxide exhibit a similar disinclination to oxidate iron. (Wöhler, *Ann. Pharm.* 28, 92.)

The black hydrate of ferroso-ferric oxide exhibits, after drying, the appearance of brown black, brittle, strongly magnetic lumps, having a conchoidal fracture and yielding a dark brown powder. It contains about 7 per cent. of water, which it gives off when heated in a retort, leaving black anhydrous ferroso-ferric oxide. When heated in the air it is converted into ferric oxide. From its yellow solution in hydrochloric acid, it is precipitated unchanged by ammonia. (Wöhler.)

Iron-black or *Æthiops martialis Lemeryi* is a mixture of ferric and ferrous oxides, in different proportions, according to the mode of preparation, and partly hydrated.

Anhydrous Æthiops is obtained by the following methods: 1. By passing aqueous vapour over red-hot iron, or sprinkling red-hot iron filings or nails repeatedly with water, till they become friable. This

method yields FeO,Fe^2O^3.—2. An intimate mixture of pulverised iron and ferric oxide is tightly pressed into a crucible, the cover put on, and the whole exposed for two hours to an intense heat. To obtain FeO,Fe^2O^3 by this process, the proportions required are 27 pts. (1 At.) iron, 312 pts. (4 At.) Fe^2O^3. Vauquelin and Bucholz, with the view of obtaining pure ferrous oxide, prescribe 95 parts (rather more than 1 At.) of ferric oxide to 27 pts (1 At.) of iron; in that case, the products must contain metallic iron.—3. Hydrated ferric oxide is mixed with a sufficient quantity of olive oil to form it into a moist powder, and then ignited in a covered crucible or in a retort. The anhydrous oxide may likewise be used instead of the hydrate, and wax or vinegar instead of oil: vinegar if used must be added in large quantity, the mixture subsequently distilled, and the residue heated to redness. The charcoal which remains on igniting these substances, serves for the partial reduction of the ferric oxide. If the quantity of organic matter is too small, part of the ferric oxide remains unaltered; if it is too great, an excess of charcoal is produced, and part of the ferroso-ferric oxide is thereby reduced to the metallic state.

Hydrated Æthiops.—1. Iron-filings are placed in a wide vessel and covered with a deep stratum of water; the whole is exposed to the air for a considerable time and frequently stirred; and the lighter black powder which forms, decanted from time to time from the remaining iron filings, then quickly collected on a filter, and rapidly dried at a moderate heat. (Lemery.) If the filings are moistened with only a small quantity of water, and the mixture agitated, the oxidation goes on much more rapidly and is attended with evolution of heat, so that it becomes necessary to replace the water as it evaporates; after five days the æthiops may be removed by levigation. (Cavezzali.) This preparation is doubtless identical with the black hydrate of ferroso-ferric oxide already described (p. 192), and the much more expeditious modes of forming it, recommended by Preuss and Wöhler, are to be preferred.

b. With Acids, forming the SALTS, OF FERROSO-FERRIC OXIDE, or FERROSO-FERRIC SALTS.—These salts are obtained by partial oxidation of ferrous salts, or partial de-oxidation of ferric salts, or by mixing ferrous salts with ferric salts, or by dissolving ferroso-ferric oxide in acids. They are mostly of a bright green, brownish, or yellow colour, and have a ferruginous taste. Like the ferrous salts, they are converted into ferric salts by oxidation. Many oxidable substances, on the contrary, such as sulphuretted hydrogen, metals, &c., convert them into ferrous salts by withdrawing a portion of their oxygen. They may be regarded as mere mixtures of ferrous with ferric salts, and exhibit many reactions belonging to one or the other of these salts. They are characterized by the green, black, or—if a large quantity of ferric salt is present—the brown-black precipitate which they form with alkalis, and the blue with cyanide of potassium. They resemble the ferrous salts in giving a blue precipitate with ferricyanide of potassium, and the ferric salts in their behaviour with meconic acid, gallic acid, hydrosulphocyanic acid, and ferrocyanide of potassium.

D. FERRIC OXIDE. Fe^2O^3.

Sesquioxide of Iron, Peroxide of Iron, Red Oxide of Iron. Occurs in the forms of *Specular Iron* or *Iron-glance, Red Hæmatite* or *Red Iron-stone,* and *Martite.*

Preparation. 1. By igniting the metal or ferroso-ferric oxide for a considerable time in contact with air: [illegible] *M* [illegible]—2. By igniting hydrated ferric oxide.—3. By strongly igniting calcined green vitriol, or disulphate of ferric oxide: [illegible] *M* [illegible].—4. By oxidating iron with nitric acid, then evaporating to dryness and igniting.—5. By deflagrating 1 part of iron filings with three parts of nitre, and extracting the potash with water: [illegible] *M* [illegible] *Zeitschr.*

Properties. The primary form of specular iron is an acute rhombohedron, *Fig.* 151; also *Figs.* 153. 155. 156. 157: [illegible] or r^3=92° 5'; somewhat cleavable parallel to [illegible]. Hardness. Sp. gr. 5·21 (Mohs); 5·19...5·23 G. Rose. Softer than quartz: steel-grey, yielding a brown-red powder. In thin laminæ, as it occurs in micaceous iron-ore, it transmits light of a red colour. Red hæmatite is generally of fibrous texture, less hard, of brown-red colour, and mostly has a density of 4·7. —Martite, although it consists of pure ferric oxide, crystallizes in regular octohedrons, probably therefore exhibiting a case of dimorphism. (Kobell, *Schw.* 62, 196.)—Artificial ferric oxide, obtained by strong ignition of the sulphate or nitrate, is steel-grey and metallic; sometimes, when it is produced by heating the sesquichloride of iron in vessels containing air, it forms a sublimate consisting of laminæ, identical with those of micaceous iron-glance (*Fig.* 153, with the *p* faces enlarged): and appears red by transmitted light. The same laminæ are formed in pottery-furnaces in which the ware is glazed with common salt. (Mitscherlich, *Pogg.* 15, 630.) ¶ The specific gravity of artificial ferric oxide ignited over a spirit lamp, is 5·17; after ignition over a charcoal fire 5·04. In the pottery-furnace, it melts, but is at the same time partly converted into ferrous oxide. (H. Rose, *Pogg.* 74, 440.) ¶

			Buchholz.	Gay-Lussac.	Stromeyer.	Berzelius.	Dobereiner.	Thomson.
2Fe	54	69·23	70·42	70·27	69·85	69·22	69	68·965
3O	24	30·77	29·58	29·73	30·15	30·78	31	31·035
Fe^2O^3	78	100·00	100·00	100·00	100·00	100·00	100	100·000

(Fe^2O^3 = 2 . 339·21 + 300 = 978·42. Berzelius.)

Decompositions. 1. By gentle ignition with charcoal, it is reduced to ferroso-ferric oxide; by stronger ignition, to the metallic state.—Ferric oxide, heated to whiteness in a charcoal crucible, yields metallic iron at the part which is in contact with the charcoal lining, but not till the rest of the oxide, to the very centre, is reduced to the state of ferroso-ferric oxide. (Berthier.) This reduction of the part of the oxide not in contact with the charcoal, to the state of ferroso-ferric oxide, is due to the action of carbonic oxide gas. If two platinum crucibles, the one containing a piece of charcoal, the other a piece of iron-glance, be placed at a distance from one another in a porcelain tube closed at one end, and the whole ignited, carbonic oxide and carbonic acid gases are evolved, and the iron-glance reduced to the metallic state. For the oxygen of the air in the tube combines with the charcoal and forms carbonic oxide gas, which is converted into carbonic acid by the ferric oxide, and subsequently brought back to the state of carbonic oxide by the charcoal, and so on. If the tube is filled with nitrogen gas, the reduction is much slower; in this case, the small quantities of oxygen and hydrogen in the charcoal, which are set free in the forms of carbonic oxide and hydrogen gas, serve to induce the reduction. (Leplay & Laurent, *Ann. Chim. Phys.*

65, 403; also *J. pr. Chem.* 13, 284.) — The peculiar circumstance in Berthier's experiment of the non-production of metallic iron till all the ferric oxide had been converted into ferroso-ferric oxide, cannot be explained by the penetration of carbonic oxide gas from the carbonaceous envelope to the interior; for carbonic oxide could not penetrate the ferroso-ferric oxide without reducing it to the metallic state; the reduction must therefore be a transposition of atoms, like that which occurs in galvanic decompositions, whereby the oxygen of the ferric oxide is transferred from the interior towards the carbonaceous envelope. For copper, likewise, when surrounded with cupric oxide and ignited, is converted, even to a considerable depth, into cuprous oxide, to which state the cupric oxide is also reduced,—and this effect takes place without the co-operation of any gas. (Degen, *Ann. Pharm.* 29, 261.) — Becquerel (*Ann. Chim. Phys.* 49, 131) likewise supposes a galvanic motion of this nature to take place in Berthier's experiment.

Since, according to Laurent (*Ann. Chim. Phys.* 65, 404), carbonic oxide gas, mixed with an equal volume of carbonic acid, merely reduces ferric oxide to ferroso-ferric oxide, the explanation of Leplay & Laurent may still hold good, if we are at liberty to suppose that the diffusion of the gases in the pulverulent mass of ferroso-ferric oxide takes place quickly enough to transfer the carbonic acid gas produced in the interior towards the charcoal envelope, in quantity sufficient to interfere with the reducing action of the carbonic oxide which diffuses itself from without inwards,—that reducing action, moreover, being in itself but feeble.— Ferric oxide ignited with carbonate of soda on charcoal before the blowpipe, sinks, together with the carbonate of soda, into the charcoal, and is easily reduced to a metallic powder, which may be separated from the charcoal by pounding and levigation. (Berzelius.)—2. A stream of carbonic oxide gas reduces ferric oxide heated to redness in a tube, first to ferroso-ferric oxide, and afterwards to the metallic state. (Göbell, *J. pr. Chem.* 6, 386; Gm.)—Proust (*Scher. g.* 10, 113; also *Gilb.* 25, 16) and Nasse (*Schw.* 46, 73) found ferric oxide reduced to the metallic state in a pottery furnace, doubtless by the action of carbonic oxide gas.—Proust also found that ferric oxide was reduced to ferroso-ferric oxide when ignited in crucibles (into which the carbonic oxide from the fire could penetrate), but not when heated in a coated retort.—3. Hydrogen gas acts like carbonic oxide. The reduction begins somewhat above the boiling point of mercury. (Magnus.)—Ammoniacal gas likewise reduces ferric oxide to the metallic state.—4. Ferric oxide ignited with sulphur yields sulphurous acid and sulphide of iron.—It is not reduced by a boiling solution of protochloride of tin. (A. Vogel. *Kastn. Arch.* 23, 85.)

Combinations. *a.* With Water. HYDRATED FERRIC OXIDE, or FERRIC HYDRATE.—Found native in the form of *Brown Iron-ore, &c.* Many kinds of brown iron-ore appear to be formed by the deposition of hydrated ferric oxide from water containing ferrous carbonate in solution, as it issues out of the earth and evaporates in the air. If this water gives off its carbonic acid out of contact of air, it deposits monocarbonate of ferrous oxide in the form of *Sphærosiderite.* (Bischoff, *Schw.* 68, 420.) Much hydrated ferric oxide has likewise been produced by the action of the air on ferrous carbonate and sulphide of iron.—*Preparation.* 1. By exposing iron moistened with water to the air for a considerable time: *Iron-rust, Crocus Martis aperitivus.*—2. By exposing hydrate or carbonate of ferrous oxide, obtained by precipitating green

vitriol with a caustic alkali or alkaline carbonate and afterwards washed, to the air while yet moist.—3. By precipitating a ferric salt with excess of caustic alkali or alkaline carbonate. According to Berzelius, the precipitate thereby obtained always contains more or less of the alkali employed.—The native hydrate is brown or yellow, crystallized in thin tables, capillary, fibrous, compact, conchoidal or ochrey.—Iron-rust and the hydrate obtained by (2) are yellowish-brown, friable, earthy masses. The hydrate precipitated by ammonia dries up to a compact brown mass having a shining, conchoidal fracture.—If any of the looser varieties of the hydrate, either natural or artificial, are gently heated (not to redness) so as to expel the water, and the remaining oxide is then more strongly heated, it becomes incandescent without further loss of weight, and is afterwards less soluble in acids. (Berzelius.)

There are several varieties both of the native and of the artificial hydrate, differing not only in external appearance, but likewise by the quantities of water which they contain. According to the analyses hitherto given, the following varieties may be distinguished:

α. Fe^2O^3,HO.—To this head belong: *a. Needle iron-ore* from Oberkirchen. (It is amorphous with Manganite [IV, 203] of specific gravity 4·32, and contains 10 per cent. of water: *Breithaupt.*)—*b. Göthite* (*Pyrosiderite, Ruby mica*) from Eisenfeld in Nassau.—*c. Lepidokrokite* from the Hollertenzug in the Westerwald. (In a specimen of this mineral from Hamm, Breithaupt found 14·32 per cent. of water, and in one from Baden 13·49 per cent.)—*d. Brown Iron-ore* from Saxony in pseudo-crystals of iron-pyrites. According to Kobell (*J. pr. Chem.* 1, 181) the brown Hæmatite from Maryland and that from Beresof have a similar composition.—*e.* The same from Orenburg. (The so-called mineral hailstones.)

			Kobell.				Hermann.
			a.	*b.*	*c.*	*d.*	*e.*
Fe^2O^3	78	89·65	90·53	86·35	85·65	86·34	90·02
HO	9	10·35	9·47	11·38	11·50	11·66	10·19
SiO^2			trace	0·85	0·35	2·00	
CaO				trace	trace		
Mn^2O^3				0·51	2·50		
CuO				0·91			
Fe^2O^3,HO	87	100·00	100·00	100·00	100·00	100·00	100·21

β. $2Fe^2O^3,3HO$.—*a. Fibrous Brown Iron-ore* or *Brown Hæmatite* from Viedessos.—*b.* The same from Kamensk.—*c.* The same from Horhausen. According to Breithaupt, brown hæmatite contains on the average 39·59 per cent. of water, and likewise a small proportion of silica which remains as a gelatinous residue when the mineral is dissolved in acids, and appears to be an essential constituent of fibrous brown iron-ore.—*d.* Compact *Brown iron-ore* from Pr. Minden, in pseudo-crystals of iron-pyrites.—*e.* Iron-rust, prepared according to (1).

			Daubisson. *a.*	Kobell. *b.*	Schonberg. *c.*	Kobell. *d.*	Berzelius. *e.*
$2Fe^2O^3$	156	85·24	82	83·38	82·27	82·24	85·3
3HO	27	14·76	14	15·01	13·26	13·26	14·7
SeO^2			1	1·61	4·50	4·50	
Mn^2O^3			2				
$2Fe^2O^3,3HO$	183	100·00	99	100·00	100·03	100·00	100·0

γ. $Fe^2O^3,2HO$.—*a*. Violet-brown fibrous brown iron-ore from Raschau; sp. gr. 3·34.—*b*. The hydrate precipitated by ammonia from ferric hydrochlorate and dried at 100°. The loss by ignition may arise from a small quantity of ammonia as well as water.—*c*. The same dried in the sun (the composition of this nearly corresponds to the formula $Fe^2O^3,3HO$).

				Breithaupt. *a*.	Gm. *b*.	Berthier. *c*.
Fe^2O^3	78	81·25		80·3	81·49	72
2HO	18	18·75		19·7	18·51	28
$Fe^2O^3,2HO$	96	100·00		100·0	100·00	100

¶ According to Schaffner (*Ann. Pharm.* 51, 117), the hydrate obtained by precipitating hydrochlorate of ferric oxide with ammonia, contains 89·74 p. c. ferric oxide and 10·26 water, numbers which agree with the formula Fe^2O^3+HO. The same hydrate is also formed by exposing ferrate of potash to the air. According to Wittstein (Buchner's *Repert.* 43, 367), hydrated ferric oxide, when first precipitated, contains 3 atoms of water, $Fe^2O^3,3HO$, and in that state is easily soluble in acetic or citric acid, and when examined by the microscope presents the appearance of an amorphous powder. But after being kept for some time under water, it acquires a crystalline structure, and becomes much less soluble in acids. In this state, it is found to contain half as much water as before, being, in fact, composed of $2Fe^2O^3,3HO$. ¶

b. With Acids, forming the Salts of Ferric Oxide, or Ferric Salts.—*Per-salts of Iron*.—The affinity of ferric oxide for acids is much less than that of ferrous oxide. Crystallized and ignited ferric oxide dissolves very slowly in acids; the hydrate dissolves easily. Ferric salts are likewise produced by exposing ferrous and ferroso-ferric salts to the air, or by heating them with nitric acid, or by bringing them in contact with chlorine-water, or with other bodies containing oxygen; also by dissolving iron in nitric acid, or in another acid mixed with nitric acid and heated.—The dehydrated salts of ferric oxide containing 3 atoms of acid are mostly white; the hydrated and the more basic salts are generally brown or brownish-yellow; those which are soluble have an inky taste, more astringent than that of the ferrous salts. They give off their acid, if it is volatile, at a red heat, and exhibit before the blowpipe all the reactions of ferric oxide. One atom of ferric oxide requires 3 atoms of acid to form a normal salt, and the salts thus formed are for the most part soluble in water, and when dissolved, redden litmus. Many of these solutions, when deprived of part of their acid by an alkali, acquire a darker red-brown colour, and if subsequently boiled, deposit hydrated ferric oxide or a basic salt. (Herschel, *Pogg.* 25, 628.) The ferric oxide is precipitated in greater quantity as the solution is more dilute. If, for example, ammonia be added to a dilute solution of a ferric salt, till the liquid is perfectly neutral, ferric oxide is deposited on the application of heat; and if the liquid be again neutralized after cooling, it will yield a fresh precipitate of ferric oxide when heated—and so on, till all the oxide is precipitated. The complete precipitation of the ferric oxide may be at once effected by heating the iron solution to the boiling point, and mixing it with dilute ammonia till it no longer reddens litmus, or till it acquires a very slight alkaline reaction; under these circumstances, the protoxides of manganese, nickel, cobalt, and likewise of cerium, are retained in solution. (Herschel, *Phil. Trans.* 1821, 293; also Ann. Chim. *Phys.* 20,

304; abstr. *Schw.* 32, 452.) The solution may also be neutralized with potash, then largely diluted and boiled. A solution of the sulphate is best adapted to the purpose, because the basic sulphate of ferric oxide, which is at first precipitated, is insoluble in water, whereas the basic hydrochlorate is slightly soluble, and the basic nitrate more so. (M. Sheerer, *Pogg.* 49, 306.) Metallic iron immersed in ferric salts protected from the air, converts them into ferrous salts: *e. g.*

$$Fe^2O^3,3SO^3 + Fe = 3(FeO,SO^3).$$

The same effect is produced by other metals, even by silver at a boiling heat, whereas, at ordinary temperatures, a ferrous salt by contact with a silver-salt is converted into a ferric salt, and silver is precipitated in the metallic state (I. 132)—Phosphorous acid converts ferric into ferrous salts, with formation of phosphoric acid, slowly in the cold, immediately on the application of heat. (Berthier, *Ann. Chim. Phys.* 50, 363) Phosphoric oxide forms a white precipitate with hydrochlorate of ferric oxide. (Leverrier.)—Sulphurous acid reduces ferric salts to the state of ferrous salts with great facility, especially if the solution is heated. (A. Vögel, *J. pr Chem.* 29, 281.) The effect observed by R. Phillips (*Phil. Mag. J.* 2, 75), that sulphurous acid imparts to ferric sulphate a deep red colour which disappears in a few hours without reduction of the salt, must be attributed to the presence of nitric acid, inasmuch as he used green vitriol oxidized by boiling with nitric acid.—Protochloride of tin likewise reduces ferric to ferrous salts; so also does trithionic acid. (Persoz.)—A dilute solution of ferric chloride imparts a blue colour to an alcoholic solution of guiac-resin. (Unverdorben.)—Hydrosulphuric acid converts ferric salts which contain one of the stronger acids into ferrous salts, with precipitation of sulphur. In a solution of the hydrochlorate (but not in the acid acetate) a small quantity of sulphuric acid is produced, even in the cold. (H. Rose, *Pogg.* 47, 161.) If the ferric oxide is dissolved in a weaker acid, sulphuretted hydrogen throws down a black precipitate of hydrated sesquisulphide of iron: *e. g.*, from the solution of ferric oxide in vegetable acids, such as acetic acid, when the acid is not in excess; or from a solution of the oxide in a mineral acid mixed with acetate of soda; part of the iron, however, always remains dissolved in the form of ferrous oxide. (Wackenroder, *N. Br. Arch.* 16, 118.) Alkaline hydrosulphates precipitate the iron completely—in the form of black hydrated sesquisulphide, if the iron-salt is poured into an excess of the alkaline hydrosulphate, but as a mixture of hydrated sesquisulphide and sulphur, in the contrary case. The precipitated sesquisulphide is insoluble in excess of the alkaline hydrosulphate; if, however, the solution is very dilute, a small quantity of the sulphide remains dissolved, imparting a green colour to the liquid (H. Rose), and is deposited on exposure for some time to the air, or on the addition of hydrosulphite of ammonia. (Wackenroder.) The precipitated sulphide acquires a rusty brown colour when exposed to the air; it dissolves easily in mineral acids, but not in acetic acid. (Wackenroder.)—An aqueous solution containing not less than 1 part of iron in 100,000 parts of water gives a black precipitate with hydrosulphate of ammonia; with 200,000 parts of water, a dark green mixture is produced; with 400,000 pts. a greyish-green; and with 800,000 pts. of water, a greyish-green colour after a few minutes. A similar effect is produced by bihydrosulphate of potash. (Roth, *Repert.* 47, 368.) Hyposulphite of soda produces with ferric salts a blackish-red colour, which disappears in a few hours, the ferric salt being reduced to the ferrous

state. (Lenz, *Ann. Pharm.* 40, 101.) The red colouring is produced even when the liquid is quite free from nitric acid, and it disappears in a few seconds. (Gm.) The hydrated sulphides of manganese, cobalt, and nickel throw down sesquisulphide of iron from a solution of ferric hydrochlorate. (Anthon.)

All caustic alkalis added in sufficient quantity to ferric salts, throw down yellowish-brown flakes of hydrated ferric oxide, which, according to Berzelius, carries more or less of the alkali down with it, and is insoluble in excess of the alkali. ¶ According to Schaffner, hydrated ferric oxide precipitated by ammonia is perfectly free from that alkali, so that when it is ignited with carbonate of lead-oxide in a tube, the gas which escapes passed into hydrochloric acid, and the liquid afterwards treated with chloride of platinum, not a trace of chloroplatinate of ammonium is obtained.—According to Wittstein, hydrated ferric oxide is slightly soluble in strong caustic potash; Schaffner, on the other hand, is of opinion that the oxide supposed to be dissolved by the potash is merely in a state of fine mechanical suspension ¶.—The monocarbonates of ammonia, potash, and soda, and likewise the bicarbonates, yield the same precipitate as the caustic alkalis; it is, however, of a lighter brown colour (becoming darker on boiling); contains a small quantity of carbonic acid; and if the liquids are somewhat concentrated, dissolves in excess of the alkaline carbonate, forming a red-brown solution. The precipitate is not dissolved on passing chlorine gas through the liquid. (Wackenroder.)—The carbonates of baryta, lime, magnesia, manganous oxide, zinc-oxide, and cupric oxide, likewise precipitate ferric oxide completely, even at ordinary temperatures; any ferrous oxide that may perchance be present remains dissolved, unless the liquid is heated to the boiling point. (Fuchs, *Schw.* 62, 184; *v.* Kobell. *J. pr. Chem.* 1, 80.) Carbonate of strontia acts in the same manner. (Demarçay, *Ann. Pharm.* 11, 240.)—Phosphate of soda throws down white phosphate of ferric oxide (even to the fifteen-hundredth degree of dilution: *Pfaff*) which turns brown when treated with ammonia, and, if the phosphate of soda is in excess, dissolves in ammonia, forming a red-brown solution. — Arseniate of soda throws down white arseniate of ferric oxide (even when the solution is diluted 20,000 times: *Pfaff*).—A solution of ferric hydrochlorate mixed with acetate of soda or formiate of potash, deposits the whole of the iron, on boiling, in the form of a precipitate which re-dissolves as the liquid cools, or on being washed with cold water. (Liebig, *Ann. Pharm.* 17, 51.)—Alkaline succinates and benzoates, give a light reddish-brown precipitate with ferric salts (up to the 5000th degree of dilution: *Pfaff*), provided no excess of acid is present.—Tincture of galls imparts a bluish-black colour to ferric salts, and then precipitates them. With ferric hydrochlorate the precipitation takes place up to the 120,000th degree of dilution (*Pfaff*); with 1 part of iron in 200,000 parts of the solution, a bluish-black tint is still produced; with 1 pt. of iron in 400,000 pts. of the solution, a greenish blue; and with 800,000 pts. of water, the last-mentioned colour appears after a few minutes. (Roth.) The limit of the reaction is attained when 1 part of ferric oxide (in the state of sulphate) is contained in 300,000 parts of the solution. (Hartig, *J. pr. Chem.* 22, 51.) If the iron-salt contains an excess of one of the stronger acids, no precipitation takes place unless acetate of potash is added; the bluish-black precipitate dissolves in hydrochloric acids, and acquires a dark purple-red colour on the addition of a small quantity of ammonia.—Meconic acid and alkaline meconates impart a bright red colour to ferric salts.—Alkaline indigotates

produce the same effect (Pfaff); so likewise does free indigotic acid. (Gm.) Hydrosulphocyanic acid and soluble sulphocyanides impart a blood-red colour to concentrated solutions of ferric salts, and a reddish-yellow to dilute solutions. This colouring is produced in solutions of sesquichloride of iron to the 20,000th degree of dilution. (Pfaff.) 1 part of iron in the form of sesquichloride dissolved in 25,000 parts of water exhibits a red colour; in 200,000 pts. an orange; in 800,000 a very pale orange; and in 1,600,000, a scarcely perceptible yellow. Hydrosulphocyanic acid is therefore the most delicate of all tests for ferric salts. (Roth.) The colouring is not destroyed by hydrochloric acid unless the acid is in very great excess.—Ferrocyanide of potassium added to ferric salts throws down Prussian blue. The effect is apparent to the 100,000th degree of dilution (Pfaff); with 1 pt. of ferric oxide (in the form of sulphate) dissolved in 420,000 pts. of water. (Hartig, *J. pr. Chem.* 22, 51.)—The precipitate is insoluble in hydrochloric acid.—Oxalic acid produces a yellowish colour in ferric salts, but without precipitation.—All ferric salts which are not soluble in water either dissolve in hydrochloric acid or are decomposed by it. They are not soluble in solution of sal-ammoniac. (Brett.)

¶ Ferric salts are reduced to the state of ferrous or ferroso-ferric salts by many vegetable substances, *e. g.* fresh grass, the green branches of trees and shrubs, hay, wood-shavings, saw-dust, peat, and coal effect the reduction at ordinary temperatures; sugar, starch, gum, alcohol, turpentine, and shreds of paper, at a boiling heat. (Stenhouse, *Ann. Pharm.* 51, 284.) ¶.

Ferric Acid. FeO^2 ?

Known only in combination with certain bases, as potash, soda, and baryta, with which it forms red salts (see these salts, especially *Ferrate of potash*).

Iron and Hydrogen.

Ferruretted Hydrogen Gas ?—Hydrogen gas prepared by dissolving iron in dilute sulphuric acid contains a small quantity of iron, which it deposits after a while on the sides of the containing vessel in the form of a brown powder. (Thomson, *System of Chemistry.*)—If the gas evolved on dissolving iron-wire, filings, or nails in dilute hydrochloric or sulphuric acid, be passed through four bottles filled with potash-solution, and through a tube filled with asbestos, in order to retain any iron salt mechanically carried over, it still retains iron and a small quantity of phosphorus, although when passed through re-agents for detecting iron, it exhibits none of the usual characteristics. It must be regarded as hydrogen gas containing small quantities of ferruretted and phosphuretted hydrogen.—It has a metallic odour, likewise resembling that of garlic. When ignited at the orifice of a tube, it burns with a flame which is yellow at the circumference and green in the interior, and deposits rusty brown and often iridescent spots on a porcelain capsule held before it; the gas prepared with hydrochloric acid deposits these spots more abundantly than that obtained with sulphuric acid. The spots disappear immediately in chlorine gas, and dissolve in nitric acid, forming a ferric salt. Strong nitric acid through which the gas has been passed for some hours, is found to

contain small quantities of ferric oxide and phosphoric acid. Aqueous chlorine, iodine, and bromine decompose the gas, and take from it a small quantity of iron. From aqueous solutions of mercurous, silver, and gold salts, the gas precipitates the respective metals. When passed through a solution of corrosive sublimate, it throws down a white or yellowish-white precipitate, and afterwards burns with a pale-yellowish flame, without depositing spots upon porcelain.—The gas obtained with English steel-wire is somewhat different. Its odour is more empyreumatic, but metallic, and not all like garlic [probably because it contains no phosphorus]. It burns with a yellow flame without any mixture of green, forms fewer spots on porcelain, and these spots have more of the metallic appearance of iron. The burnt odour, which perhaps arises from the presence of a hydro-carbon, is not destroyed by washing the gas with a solution of corrosive sublimate or silver-nitrate. (Dupasquier, *Compt. rend.* 14, 511; also *N. J. Pharm.* 1, 391; also *J. pr. Chem.* 26, 184.)—¶ According to Schlossberger & Fresenius (*Ann. Pharm.* 51, 413), the spots which this so called ferruretted hydrogen deposits on a porcelain plate contain not a trace of iron, but consist of certain compounds of phosphorus, most probably phosphoric oxide mixed with phosphoric acid; they volatilize with tolerable facility, are insoluble in hydrochloric acid, but soluble in aqua-regia. The gas from which these spots were obtained was purified by passing through two wash-bottles containing distilled water, and then through a tube 4 feet long, half filled with moist and half with dry cotton. When the gas thus purified was passed through a solution of corrosive sublimate, it threw down a copious yellowish-white precipitate, which was found to contain mercury, chlorine, phosphorus, and sulphur, but not the smallest quantity of iron. Hence the authors conclude that the gas evolved by the action of dilute sulphuric or hydrochloric acid upon iron is mixed with small quantities of phosphuretted and sulphuretted hydrogen, which produce the reactions just mentioned, but is perfectly free from iron, and consequently that *the existence of ferruretted hydrogen is not established.* ¶

Iron and Carbon.

A. Carbide of Iron.—Iron enters into combination with carbon: 1. In the reduction of iron-ores by excess of carbon at a heat reaching to the melting point: *Cast-iron, Iron-assays.* 2. When iron is fused in contact with charcoal or diamond. A small well-closed iron crucible containing a diamond, and inclosed in two well-covered earthen crucibles, fused together with the diamond at the heat of a blast-furnace, and was converted into steel. (Morveau & Clouet, *Scher. J.* 4, 170; also *Gilb.* 3, 65; Mackenzie, *Scher. J.* 5, 366.) Charcoal or graphite acts upon iron in the same manner.—3. Iron ignited slowly, and only to the softening point, in contact with carbonaceous matter, takes up carbon, which, gradually penetrating from without inwards, converts the iron, first into steel, and then into a compound similar to cast-iron:—*Cementation of iron.*—If the ignition is not continued long enough to complete the process, a nucleus of softer iron remains in the middle.—This union of iron with carbon takes place when the iron is surrounded with vegetable or animal charcoal, with coal-gas, and even with cast-iron. Iron surrounded with *cast-iron turnings* is converted into a steel at a lower red heat than when *it is immersed* in charcoal powder. Graphite under the same circum-

stances does not form steel. (Gaultier, *J. Pharm.* 13, 18.) An iron-wire immersed in melted cast-iron, which is kept at a red heat for four hours after solidification, is found to be converted into steel. (Degen.)

The outermost layer of iron takes up the carbon with which it is in contact, transfers it to the next layer, and so on, till the carbon is disseminated throughout the whole mass. In a similar manner, iron rich in carbon is converted by ignition in contact with air, *e. g.* in the refining process—into wrought-iron, although the air does not come in contact with all the particles; the carbon, in fact, travels from within outwards till equilibrium is established. (Berzelius, *Jahresber.* 18, 160.)—The atoms of iron which have combined with carbon at the surface, turn half-round, give up their carbon to the iron-atoms immediately within, take up another portion at the surface,—and so on, till the two substances have penetrated one another completely. At a red heat, the iron is sufficiently softened to allow this rotation of the atoms. (Becquerel.) Degen likewise admits the probability of a galvanic movement of this kind.—Leplay & Laurent suppose that the carbonization of the iron is due to the action of carbonic oxide gas, which is produced by the ignition of the charcoal, and penetrates the softened metal, giving up part of its carbon to the iron, and being thereby converted into carbonic acid gas. At all events, they found that when charcoal and iron placed in two separate little porcelain boats, were heated to whiteness in a porcelain tube, the iron was converted into steel containing 0·7 per cent. of carbon; nevertheless, they admit that this effect might be due to the carburetted hydrogen gas evolved from the charcoal, especially as no carbonization of the iron took place if the charcoal had been very strongly ignited before the experiment, or when pure carbonic oxide was passed over red-hot iron.—More recently Laurent has put forth the view, that the carbon volatilizes at the cementing heat, and penetrates the iron in the form of vapour; and moreover, that the carburetted hydrogen gas evolved from fresh wood-charcoal, and the cyanogen evolved from animal charcoal, may likewise contribute to the carbonization of the iron. (*Ann. Chim. Phys.* 65, 403 and 417; also *J. pr. Chem.* 13, 284 and 295.) The observations which Laurent adduces in favour of this theory, do not, however, establish the volatilization of carbon at so low a red-heat; and even if carbon vapour were produced, the carbon would be deposited from it only on the surface of the iron, and could not penetrate the metal in the gaseous form: for, Laurent's assumption that iron when softened by ignition is permeable to gases, is contradicted by the fact that bubbles are produced in the interior of the iron during cementation—consisting of carbonic oxide gas formed in places where the carbon, as it penetrates the iron, comes in contact with scale-oxide—and these bubbles are unable to escape through the pores of the iron. (Degen, *Ann. Pharm.* 29, 251.)

According to Karsten's observations, carbon appears to exist in combination with iron in three different ways: 1. Combined with the whole of the iron (iron completely saturated with carbon at the melting point appears to be Fe^4C); – 2. Combined with part of the carbon, forming ter-carbide of iron, FeC^3, which compound is diffused throughout the rest of the iron;—3. In the free state, forming laminæ of *graphite*,—being, in fact, carbon free from iron, separated by slow cooling from a mass of iron saturated with carbon at the melting heat.—The more quickly iron combined with carbon is cooled after fusion or ignition, the greater is the quantity of carbon which remains combined with the whole of the iron; the slower the cooling, the greater is the quantity of FeC^3 produced,—and if

the iron has been more fully saturated with carbon at the melting point—as in the case of cast-iron—the greater is the amount of carbon which separates completely in graphite-laminæ. Hence, the properties, and in particular, the hardness of carburetted iron, depend not merely on the proportion of carbon, but more especially also, on the peculiar manner in which that substance is combined with it. The greater the quantity of carbon in combination with the whole of the iron, the harder is the compound, and the more completely does it resist rusting and the action of acids.

The three states of the carbon in carburetted iron may be distinguished by the appearances presented on treating the compound with acids:

1. Carbon in combination with the whole of the iron. During the solution, especially of rapidly-cooled steel and white pig-iron, an offensive kind of hydrogen gas containing carbon is evolved, and a volatile oil and a brown mouldy substance are produced. The hydrogen gas derives its carbon and its odour principally from the volatile oil, part of which, however, remains behind with the mould, and is not completely expelled till after long boiling with the acid. [Whether the hydrogen gas likewise contains carbon in another form of combination—*e. g.* as marsh-gas, as is sometimes supposed—is, in my opinion, not established by any definite experiment; on the other hand, according to Proust (*N. Gehl*, 3, 395) 1 volume of the gas evolved by cast-iron, although heavier than air, consumes only half a volume of oxygen when detonated with 2 volumes of that gas,—probably because the oily vapour remains unburnt.] The mould forms a black-brown porous mass, which after washing and drying, dissolves in potash, forming a black-brown solution, and when heated, burns with an odour of peat, without leaving any ferric oxide. The formation of the oil appears to depend upon this circumstance, that while the iron combines with the oxygen of the water, part of the hydrogen, while *in the nascent state* unites with a portion of the carbon which was in combination with the whole of the iron, and produces the oily substance. In the formation of the mould, not only hydrogen from the water, but likewise a portion of the water itself (or its elements) appears to unite with another part of the carbon which was combined with the whole mass of iron, and thereby convert it into mould.—When nitric acid or aqua-regia is made to act on hardened steel or white pig-iron, no oil is formed, and instead of the black-brown mould, a red-brown substance of similar character is formed, which partly dissolves in the nitric acid liquid, imparting to it a brownish-yellow colour. This red-brown mould is probably distinguished from the black-brown by containing one of the oxides of nitrogen, and perhaps also by a larger proportion of oxygen.

2. FeC^3. When dilute sulphuric or hydrochloric acid acts upon slowly cooled bar-iron (which always retains a small portion of carbon) or on slowly cooled steel or on grey pig-iron—the action not being allowed to go on too long—there remains (besides the mould, which may be dissolved out by caustic potash), a graphite-like, but magnetic mass, which, if burnt after washing and drying, leaves from 82 to 94 per cent. of ferric oxide, and is probably therefore FeC^3. (Karsten.) [$FeC^3 = 27 + 18 = 45$; consequently 100 parts of it contain 60·87 per cent. of iron, and these yield 86·96 p. c. of ferric oxide.] Bromeis doubts the existence of FeC^3 in carburetted iron; at all events, he remarks, *when this* carburetted iron is dissolved in acids, the residual graphite *often contains* very variable quantities of iron; sometimes, however,

because the action of the acid has not been continued long enough; sometimes from admixture of phosphide or silicide of iron with the graphite. But why should the graphite, in which the presence of iron is stated to be merely accidental, be converted by the continued action of hydrochloric acid into black-brown, and of nitric acid into red-brown mould?

3. *Graphite.* Remains undissolved, together with FeC^3, when grey pig-iron is dissolved in acids.—In consequence of the separation of mould, FeC^3, and graphite, a dark spot is produced upon carburetted iron by the action of acids, especially of nitric acid.

a. Bar-iron, Refined Iron, Malleable Iron, Wrought Iron.—All iron manufactured on the large scale contains a certain portion, not exceeding 0·5 per cent. of carbon, which gives it greater solidity and thereby renders it better adapted for the majority of purposes. *Burnt Bar-iron* is the only variety that is free from carbon. Soft bar-iron contains less than hard. Bar-iron is distinguished from steel, which is richer in carbon, by not becoming brittle or sensibly harder when rapidly cooled in water after ignition.

In very dilute hydrochloric or sulphuric acid, bar-iron dissolves very slowly, leaving black, magnetic, graphite-like FeC^4, which is converted by nitric acid into brown mould, takes fire even below a red heat, and burns without leaving a residue.—Stronger sulphuric acid leaves traces of easily inflammable charcoal. Strong hydrochloric acid dissolves bar-iron without leaving any residue. [Is all the carbon evolved in this case in the form of oil?]—Cold and very dilute nitric acid forms red-brown mould, which dissolves on the application of heat, imparting a brown colour to the liquid. (Karsten.)

Analyses of Bar-iron. According to Gay-Lussac and Wilson (*N. Quart. J. of Sc.* 7, 203; also *Jahresber.* 11, 128).—*a.* Best bar-iron from Sweden.—*b.* The same.—*c.* Bar-iron from Creusat.—*d.* From Champagne.—*e.* From Berry.—*f. Cold-short* bar-iron from Moselle. In 100 parts:

	a.	*b.*	*c.*	*d.*	*e.*	*f.*
C	0·293	0·240	0·159	0·193	0·162	0·144
P	0·077	trace	0·412	0·210	0·177	0·510
Si	trace	0·025	trace	0·015	trace	0·070
Mn	trace	trace	trace	trace	trace	trace

Amount of Carbon in Bar-iron. a. Soft.—*b.* Hard.—*c. d. e.* Three different varieties, produced from white pig-iron by the Swabian method of refining.—*f. g. h.* Three varieties produced from various kinds of pig-iron by the Mägdesprung method of refining. The samples *c* to *h* are from the Bernburg works. In 100 parts:

	Karsten.		Bromeis.					
	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Combined C	....	....	0·238	0·354	0·38	0·104	0·237	0·66
Free C	....	....	0·080	trace	0·02	0·220	0·260	trace
Total	0·2	0·5	0·318	0·354	0·40	0·324	0·497	0·66

Bromeis (*Ann. Pharm.* 43, 241) determined the total amount of carbon by burning with chromate of lead or chlorate of potash; the free, mechanically combined carbon or graphite was estimated by dissolving the bar-iron in hydrochloric acid and determining the quantity of carbon contained in the insoluble residue. [Could graphite really be obtained

from bar-iron containing so small a quantity of carbon, or did the insoluble residue not rather consist of Karsten's FeC^3?]

b. Steel. Preparation.—1. *Rough Steel, Refinery Steel, Natural Steel, (Frischstahl, Rohstahl, Natürlicher Stahl.)* The iron from which rough steel is made, is pig-iron containing but few foreign admixtures besides carbon and manganese. It is refined by exposure to the blast under charcoal, as in the refining of iron; but the oxidation is stopped at a less advanced stage, so that the foreign metals, and those only, may be almost completely oxidized, while a portion of the carbon may remain unburnt and in combination with the iron. As soon as the mass becomes somewhat malleable, it is formed into flat bars under a series of hammers continually diminishing in size. To obtain a uniform distribution of the carbon, the plates, after being cut into lengths and made up into bundles, are welded together and then formed into bars: *Shear-steel.* (*Gerbstahl.*)—2. *Bar-steel, Cementation-steel.* Very pure bar-iron in the form of thin bars is enclosed in boxes, troughs or pots filled with charcoal powder, and kept at a red-heat for 5 to 8 days. The carbon gradually penetrates the iron; where it meets with scale-oxide, it forms carbonic-oxide gas and raises the iron in blisters: *Blistered steel.* If the cementation is continued too long, the metal fuses together and forms cast-iron. (Buttery.) Or coal gas is passed over bars of iron heated to redness in a cast-iron tube coated with clay, whereby carbon is transferred from the gas to the metal. When a sufficient quantity of charcoal has entered into combination with the iron, the ignition is continued for some time longer, without passing any more gas over the metal, in order that the carbon may diffuse itself uniformly. If the gas is allowed to act too long, the steel fuses into cast-iron. (Mackintosh, *J. pr. Chem.* 2, 333.)—3. *Cast-steel.* Bar-steel is fused under a layer of pounded glass, sometimes without charcoal (Buttery, *Schw.* 35, 339), sometimes with 1 or 2 per cent. of charcoal added. In this process, the steel probably takes up small portions of aluminum and silicium from the crucible.—4. Iron fused at an intense heat with 2 per cent. of lamp-black yields good steel. (Bréant, *Ann. Chim. Phys.* 24, 388; also *Schw.* 40, 295.)—5. The *Indian Steel* or *Wootz*, which is distinguished by extraordinary hardness, and by the damasked surface which it acquires when acted upon by acids, is said by Faraday and Stodart (*Gilb.* 66, 169) to contain very small quantities of aluminum and sometimes also of silicium, and may be imitated by fusing the carburetted iron *d* (p. 217) with alumina, and then fusing 1 part of the carbide of iron and aluminum thus obtained with from 8 to 17 parts of cementation-steel.

Properties.—Somewhat whiter than iron. When red-hot or melted steel is slowly cooled, it becomes soft, though somewhat harder than iron, and exhibits a granular, indented, and somewhat shining fracture. The tenacity of slowly cooled steel is to that of bar-iron nearly as 13 : 10. Its granular texture is not, like that of iron, converted into the fibrous by rolling and hammering. (Karsten.) The fracture of unhardened steel is fine grained; that of steel which has once been re-melted *per se*, but not hardened, is still fine-grained and whiter than before. (Elsner.) On the contrary, when red-hot or melted steel is suddenly cooled, as by immersion in water—which process is called *Hardening*—it becomes much harder, more elastic, and more brittle than iron, the hardness increasing with the proportion of carbon. The fracture of hardened steel is more lustrous, conchoidal, and smooth, and of a lighter colour, but still appears fine-grained when examined with a magnifier. Notwithstanding its great hardness

it may be cut through by a rapidly rotating soft iron disc, because the latter becomes less strongly heated. When steel is hardened after too strong ignition, it exhibits a coarse-grained fracture, and has but little hardness or tenacity. (Karsten.) The fracture of hardened cast-steel is very fine-grained; that of cast-steel which has been once re-melted and hardened is very dense and uniform. (Elsner, *J. pr. Chem.* 20, 110.) Hardened cast-steel is harder than other kinds and takes a better polish.

Hardened steel when heated to redness and slowly cooled, is reconverted into soft steel. Hence by alternate exposure to quick and slow cooling after ignition, steel may be rendered either hard or soft. When hardened steel is raised to a temperature short of redness, it loses so much the more of its hardness and brittleness and approaches so much the more nearly to unhardened steel as the temperature is higher: *Tempering of Steel.*—According to Karsten's view, the hardness of rapidly cooled steel arises from the carbon which it contains being combined with the whole of the iron. When, on the contrary, the steel is slowly cooled, the greater portion of the carbon unites with a portion only of the iron and forms FeC^4, which remains intimately mixed with iron containing less carbon and therefore soft. It is only when steel is very rich in carbon that a portion of that element probably separates out in the form of graphite, on slow cooling.

Specific gravity of ordinary steel, 7·795; of hardened cast-steel, 7·6578; of cast-steel not hardened, 7·9288; of cast-steel which has been once re-melted *per se*—in the hardened state, 7·647—in the unhardened state, 8·0923 (Elsner); of Wooz, 7·665. (Faraday & Stodart.)—Hardened cast-steel fuses at 2402° C.; softer cast-steel at 2531°. (Degen.) The heat at which steel can be welded is lower than the welding heat of bar-iron; the melting point of steel is also much lower than that of bar-iron, but higher than that of cast-iron, being, in fact, lower as the proportion of carbon is higher. Many kinds of steel cannot be welded, because their melting point is too close to the temperature required for welding. (Karsten.) Cast-steel cannot be welded with iron, because at the welding heat, it crumbles under the hammer, like sand; nevertheless it is by no means more fusible than cementation-steel. (Buttery.)—Steel acquires the magnetic power less easily than iron, but retains it much more strongly.

Amount of carbon in Steel, in 100 parts: Rough Steel 1·25...2·3 (Karsten);—softest bar-steel approaching most nearly to bar-iron, at least 0·9 (Karsten);—harder bar-steel 1·3... 1·75 (Karsten);—white bar-steel from Elberfeld, 0·496 (0·416 combined, 0·80 in the form of graphite, *vid.* p. 204) (Bromeis);—English bar-steel 1·87 (and 0·1 silicium) (Berthier);—cast-steel 1·65 (and 0·1 silicium) (Berthier);—soft English cast-steel 0·833;—ordinary 1·0;—harder 1·11;—hardest 1·67 (Mushet);—best cast-steel from Sheffield 1·70 (0·95 combined, 0·22 free [there is an error in these numbers]) (Bromeis);—Rhenish cast-steel 1·267 (1·157 combined, 0·110 free) (Bromeis);—cast-steel 2·8 to 3·0 (Karsten); cast-steel 1·758;—the same after being once re-melted *per se* in a covered crucible 1·5776 (Böttger & Elsner);—Hausmann's steel 1·33 (and 0·05 silicum) (Berthier);—Wooz 1·5 (and 0·6 silicium) (Berthier).—According to Clouet, steel contains, on the average, 3·1 per cent. of carbon; according to Vauquelin, 0·71. In French steel, Vauquelin likewise found small quantities of silicium and phosphorus. Gay-Lussac & Wilson (*N. Quart J. of Sc.* 7, 204) found in the best English cast-steel, prepared from Swedish iron, 0·625 per cent. carbon, 0·03 silicium, and a trace of manganese; in cast-steel from

acquire a damasked surface,—probably because, in addition to ordinary steel, it contains a more highly carbonized or aluminiferous variety, which crystallizes in solidifying, and by continued forging is variously disseminated through the rest of the steel; and this latter variety being less attacked by the nitric acid remains whiter than the rest.—Perfectly hardened steel immersed in cold nitric acid of specific gravity 1·3, colours it brown-red, with a slight evolution of nitric oxide gas, and gradual separation of black, metallic-shining, non-magnetic flakes, which burn without leaving any residue of ferric oxide, dissolve in caustic potash forming a black-brown solution, and by continued action of the acid are converted into a brown-red powder. If the acid is heated, the same effects are produced, but more quickly and with considerable frothing. (Karsten.)—Steel which has not been hardened dissolves very rapidly in strong nitric acid, imparting to it a brown-red colour, due to dissolved mould, part of which substance, however, remains undissolved in the form of a brown-red powder. Previously to the formation of this mould, graphite-like laminæ (probably consisting of FeC^3) are separated, and these when burnt leave from 82 to 94 per cent. of ferric oxide (vid. p. 205). When steel which has been slowly cooled is treated in this manner, the laminæ are converted into red-brown mould, at the very moment of separation.—Soft cementation-steel dissolves very slowly in dilute nitric acid, yielding no graphite-like laminæ, but only red-brown mould, which takes fire even below a red-heat. Cast-steel dissolves still more slowly. (Karsten.)—Dilute sulphuric or hydrochloric acid dissolves steel, with evolution of fetid hydrogen gas containing an oily vapour, and separation of a graphite-like substance [probably FeC^3] which, by continued action of the acid, is converted into black-brown mould.—Hardened steel immersed in dilute sulphuric acid becomes covered with a small quantity of a black metallic powder; unhardened steel, in the same time, with eight times as much of a grey powder, which is soft, coherent, and may be cut with a knife, and appears to consist of carbide of iron,—inasmuch as, when exposed to the air, it changes colour in consequence of the iron becoming oxidated. By continued boiling with the acid, it is converted into a black powder [mould] the same as that produced by hardened steel. This substance, when heated in the air to temperatures between 150° and 200°, burns like a pyrophorus, emitting a large quantity of smoke; at higher temperatures it burns like asphaltum, with a bright flame, leaving a residue of ferroso-ferric oxide; it is likewise completely soluble in boiling nitric acid. (Faraday & Stodart, *Gilb.* 72, 256.)—Thoroughly hardened steel dissolves very slowly in dilute sulphuric or hydrochloric acid, becoming covered in the course of a few days, with black-brown mould, which is converted by nitric acid into brown-red mould. Stronger sulphuric acid when moderately heated also leaves a residue of black-brown mould, but boiling concentrated sulphuric acid dissolves the steel completely. (Karsten.) [Does the whole of the carbon in this last case go off in the form of oil or of gaseous carburetted hydrogen?]—Unhardened steel exhibits with dilute sulphuric or hydrochloric acid the same effects as wrought iron; excepting that it dissolves much more slowly, and leaves a more abundant graphite-like residue. [FeC^3.] Stronger sulphuric acid dissolves soft steel with tolerable rapidity, causing a separation of shining laminæ (FeC^3) which are afterwards converted into black-brown mould. (Karsten.) If the acid be quickly poured off, before this conversion has proceeded to any considerable extent, and the mould already formed be extracted with caustic potash, magnetic laminæ are left,

which retain their metallic aspect under water, but lose it in the air, and are quickly converted into mould by the action of acids. (Karsten.)

Steel may be made to unite with several metals by fusion. Many of these metals united with it in very small quantity, render it harder and more brittle. If the other metal is more electro-negative than the steel, and partly separates out in fine particles as the metal cools, the steel is thereby rendered more liable to rust. Moreover, all these alloys—particularly those which do not contain too much platinum—disengage a larger quantity of hydrogen from dilute sulphuric acid in a given time than pure steel, doubtless because a portion of the more electro-negative metal is laid bare by the first action of the acid, and then accelerates the solution of the iron by galvanic action. Pure steel dissolves most slowly of all in sulphuric acid; then follows that which is alloyed with small quantities of chromium; then with silver; then with gold; then with nickel; then with rhodium, iridium, or osmium; then with palladium; and lastly with platinum. The alloy of steel and platinum gives with sulphuric acid, in a given time, 100 times as much hydrogen gas as pure steel; even $\frac{1}{400}$ platinum is sufficient to produce this effect, but with $\frac{1}{200}$ ..... $\frac{1}{100}$ the action is still stronger. (Faraday & Stodart, *Phil. Trans.* 1822, 253; also *Gilb.* 72, 225.)—The greater hardness which steel acquires by fusion with these metals appears to result, not so much from their presence as from the additional fusion to which the steel must be subjected to form the alloy; at all events, silver-steel exhibits no greater hardness than steel which has been re-melted *per se*, vid. *silver*. (Elsner, *J. pr. Chem.* 20, 110.) Iron free from carbon may indeed be rendered harder by combination with phosphorus, sulphur, arsenic, &c., but such compounds do not harden by sudden cooling, or at all events but slightly. (Karsten.)

c. Ordinary Pig-iron; Cast-iron.—Obtained by the reduction of native iron-oxides by means of charcoal or coke in the blast-furnace (p. 166). It contains more carbon than steel, and is besides contaminated with various substances, particularly phosphorus, sulphur, arsenic, manganese, molybdenum, vanadium, chromium, copper, calcium, magnesium, aluminum, and silicium.

The properties of this substance vary according to the nature and the proportion of the substances combined with the iron, and likewise according to the rapidity of cooling from the state of fusion. For the most part, cast-iron exhibits a laminar or granular texture, sometimes crystallizes in octohedrons, and is more brittle, specifically lighter, and more fusible than malleable iron. At a red-heat, it is so soft that it may be cut with a saw.

Melted cast-iron, whether white or grey, yields white cast-iron by sudden cooling and grey by slow cooling. The former corresponds to hardened, the latter to unhardened steel, excepting that the steel contains less carbon. After sudden cooling, the carbon remains combined with the whole of the iron; but if the cooling be slow, the carbon has time to separate for the most part from its state of combination with the whole of the iron, partly as graphite, partly as FeC^3. (Karsten.) Part of the graphite remains diffused through the iron in scales; the rest crystallizes out. The greater the quantity of carbon in white cast-iron, the more strongly must it be heated in fusing and the more slowly must it be cooled after fusion, in order to convert it into the grey variety. On the other hand, grey cast-iron is most easily converted into white, by heating it just to the melting point [because then the cooling takes place more

rapidly throughout the whole mass]. In iron castings, those parts of the iron which have been in direct contact with the mould are of the white variety, being lighter in colour as the mould is wetter and the casting thinner; in the interior of the mass, the white iron passes imperceptibly into the grey. When fused cast-iron very rich in carbon is run into a very wide open mould, and thrown into water as soon as it has become solid on the surface, the portion which still remains fluid in the interior is converted by the rapid cooling into white iron. (Karsten.)

Although we must admit, with Karsten, that the different rate of cooling is the principal circumstance which determines the production of white or of grey cast-iron, we can nevertheless scarcely follow him in regarding it as the only cause of the difference; for the varying quantity of the other elements contained in it appears likewise to exert an influence on the result. Why is it that white and grey iron sometimes occur, and with sharp demarcation, in the same piece of iron? (*infra.*) Why is blackish-grey pig-iron so difficult to convert into white? Why does the same furnace, according to the manner in which it works, yield at the same rate of cooling, sometimes a whiter, sometimes a greyer iron? Why does fused grey pig-iron solidify in the form of white bright iron on the addition of sulphur (*infra*); and if the bright iron be distinguished merely by containing the greatest quantity of carbon, why is it not obtained by fusing pure iron with excess of charcoal? (Gm.)

Varieties of Cast or *Pig-iron*, particularly according to Karsten:

A. *White Pig-iron.*—Varies from tin-white to greyish-white; very brittle, cracking easily even by change of temperature; extremely hard, sometimes even more so than hardened steel, so that it will resist the strongest file; scratches glass easily. Fracture, sometimes laminar, sometimes lamino-radiating, sometimes finely splintered, sometimes dense and conchoidal. As the fracture changes from laminar to conchoidal, the colour likewise varies from white to greyish. Mean specific gravity, 7·5. Expands less than grey cast-iron when heated. Cannot be welded, because it becomes pasty at the very lowest welding heat. Fuses less readily than grey pig-iron. When heated to the melting point, it does not suddenly pass into the fused state, like grey pig-iron, but is converted before fusing, into a soft, pasty mass. In this variety of pig-iron, the carbon is united with the whole of the iron. Continued ignition out of contact of air, does not alter bright iron, but imparts a grey colour to those kinds of white pig-iron which are less rich in carbon, and renders them less hard and brittle. (Karsten.)

a. Bright Iron, Rough Steel-iron (*Spiegeleisen, Spiegelfloss, Rohstahleisen. Rohstahlfloss, Hartfloss*). This is the hardest of all kinds of iron; it resists the strongest file; exhibits a coarsely laminar fracture, with silver-white, specular, fractured surfaces. The most fusible of all kinds of pig-iron. Especially rich in carbon.

b. Whitish-grey Pig-iron.

c. Flowery Pig-iron (*Blumiges Roheisen, blumige Flossen*). Bluish, with a radiating, highly lustrous fracture.

d. Greyish-white Iron, having a fracture without distinct structure.

e. Porous Pig-iron (*luckiger Roheisen, luckiger Floss, Weichfloss*). Less white, with a bluish or greyish tinge with a somewhat indented racture; porous. Forms the transition to grey pig-iron and to steel.

B. *Grey Pig-iron.*—Between light grey and black. Sometimes with

a strong lustre; sometimes, when it contains considerable quantities of foreign metals, especially silicium, it is dull. Fracture granular. If the grains become flat and scaly, the iron is impure. Innumerable scales of graphite are interspersed between the particles. The grains, which resemble those of unhardened steel, consist principally of the compound of carbon with the whole of the iron: FeC^3 may, however, be mixed with them. Mean density 7·1. More or less soft and extensible, possessing these properties in a greater degree when cold than at a red heat. This kind of cast-iron would be very malleable, if it were not mixed with graphite. It may be welded, though not easily, because the welding and melting points are very close together. The more carbon it contains the more readily does it fuse, and with an equal proportion of carbon, it is less fusible than white pig-iron. Some varieties of it are as refractory as the harder kinds of cast-steel, others fuse almost as easily as *bright* iron. (Karsten.) A sample of pig-iron examined by Degen fused at 1326° C. Its passage from the solid to the liquid state takes place almost instantaneously, the melting point being higher and the fusion more sudden as the proportion of carbon is smaller. When very slowly cooled after fusion, it becomes more malleable than before; by sudden cooling it is converted into white pig-iron, the conversion being more complete as the proportion of carbon is greater. Thus *white iron* is obtained by pouring water on the iron which has been run off into the grooves and taking out the crusts of solid metal thus produced. The blackish-grey iron obtained when the furnace is working very hot, is however difficult to convert into white iron; but complete conversion may be obtained by pouring it into water in a fine stream. (Karsten.) [Is not the blackish-grey pig-iron peculiarly rich in carbon?] It is not altered by continued ignition with charcoal out of contact of air. It hardens by cooling in water after ignition. (Karsten.) When hardened, it scratches glass and resists an English file. (Bromeis.)

a. Mottled or *Mixed Pig-iron* (*Halbirtes Roheisen, geflecktes Roheisen*). A mixture of white and grey iron. In *strongly mottled* iron, little stars and spots of grey iron are found interspersed in bright or flowery iron; *weakly mottled iron* exhibits white specks on a grey ground. In *streaked iron* (*spengliches* or *streifiges Eisen*) grey iron is found above and below, and bright iron in the middle, with strong demarcations.

b. Grey, Normal Pig-iron (*Graues, gares Roheisen*). Produced when the charcoal, ore, flux, and air in the blast-furnace are in normal proportion. The slag or cinder produced under such conditions is perfectly fused, contains very little iron, is free from graphite-laminæ, sometimes vitreous and of a greenish or blue colour, sometimes crystallo-granular, laminar, and greyish-white. Normal cast-iron is of small-grained structure, and interspersed only with small graphite-laminæ; possesses great tenacity; is easily filed, turned, and bored; may even be hammered to a certain extent; does not readily crack from change of temperature; and is best adapted for most kinds of casting.

c. Black, supernormal Pig-iron (*Schwarzes, übergares Roheisen*). Produced when the blast-furnace is very hot and the supply of coke or charcoal too great. The grey, fine-grained mass then produced is abundantly intersected and superficially marked with laminæ of graphite, whereby its solidity is diminished.

Analyses of Cast or Pig-iron.—1. Smelted with charcoal. *a.* From *Belabre;—b.* from Autray;—*c.* from Beze;—*d.* from St. Dizier;—*e.* from

Sweden;—*f.* from Tredion;—*g.* from Lohe.—2. Smelted with coke:—*h.* from Firmy;—*i.* from Janon;—*k.* from Charleroy;—*l.* from England;—*m.* *Fine metal* from Firmy (*i. e.* iron from Firmy melted a second time). All the proportions are given in 100 parts. (Berthier, *Ann. d. Min.* 1833; abstr. *Jahresber.* 14, 127.)

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
C	2·95	3·5	3·05	3·6	4·2	3·6	3·50	3·0
Si	0·28	0.3	0·07	0·4	0·5	0·5	0·45	4·5

	i.	*k.*	*l.*		*m.*
C	4·3	2·3	2·2	1·7	— 1·00
Si	3·5	3·5	2·5	0·5	— 0·15

Iron smelted with coke is therefore much richer in silicium than that which has been reduced by charcoal.

a. Pig-iron from the Royal Works in the Harz, smelted with cold air; of sp. gr. 7·43; mottled.—*b.* The same, smelted with air at 250°; sp. gr. 7·166; normal and of a grey colour.—*c.* Pig-iron from Leerbach in the Harz; cold blast; sp. gr. 7·081; very grey.—*d.* The same, smelted with air at 110°; sp. gr. 7·077; very grey. The hotter the blast, the greater is the quantity of silicium which unites with the iron; the proportion of phosphorus, on the contrary, remains the same. (Bodemann, *Pogg.* 55, 485.)—*e.* Grey, soft pig-iron from the Maximilian Works at Bergen. (Fuchs, *J. pr. Chem.* 17, 166.)—*f.* Good pig-iron free from manganese, from the Leke iron-works. (Berzelius, *Scher. Ann.* 7, 221.)

	a.	*b.*	*c.*	*d.*	*e.*	*f.*
Fe	93·29	91·42	93·66	91·98	94·33	91·16
C combined	2·78	1·44	0·48	0·95	3·43	3·90
C free	1·99	2·71	3·85	3·48		
P	1·23	1·22	1·22	1·68	0·37	
S	trace	trace	trace	trace	0·12	
Ca	trace	trace				Mg 0·12
Al			trace	trace		
Si	0·71	3·21	0·79	1·91	1·75	0·25
Mn	trace	trace	trace	trace		4·57
Cr and V	trace					
	100·00	100·00	100·00	100·00	100·00	100·00

a. a. Grey pig-iron from Wales, smelted with coke, No. 1;—*b.* No. 2; *c.* No. 3;—*d.* Grey pig-iron from Franche-Comté, smelted with coke; *e.* The same from Creusat;—*f.* The same from the Champagne;—*g.* Grey pig-iron, with coke and wood, from Berry;—*h.* Grey pig-iron, with charcoal, from Nivernais;—*i.* White pig-iron, with wood, from the Champagne; *k.* The same, from the Isère;—*l.* The same, from Siegen;—*m.* The same, from Coblenz. The quantity required to make up the hundred parts is iron. (Gay-Lussac & Wilson, *N. Quart. J. of Sc.* 7, 204; also *Jahresber.* 11, 128.)

	a.	*b.*	*c.*	*d.*	*e.*	*f.*
C	2·45	2·55	1·67	2·80	2·02	2·10
P	0·78	0·44	0·49	0·35	0·60	0·87
Si	1·62	1·20	3·00	1·16	3·49	1·06
Mn	trace	trace	trace	trace	trace	trace

	g.	*h.*	*i.*	*k.*	*l.*	*m.*
C	2·32	2·254	2·324	2·636	2·69	2·44
P	0·19	1·013	0·703	0·280	0·16	0·19
Si	1·92	1·030	0·840	0·260	0·23	0·23
Mn	trace	trace	trace	2·149	2·59	2·45

In the following investigations, only the proportion of carbon in the pig-iron was determined; *a.* Grey pig-iron from Sain, reduced from Brown Iron-ore with charcoal.—*b.* The same, from Widdenstein in Siegen, reduced from Brown Iron-ore and Spathic Iron-ore by charcoal; *c.* The same from Malapan in Silesia, reduced from Sphærosiderite by charcoal.—*d.* The same from the Royal Works in Silesia, obtained from Ochery Brown Iron-ore by coke.—*e.* The same, but with a less hot working of the furnace. (Karsten, *Schw.* 68, 182.)—Pig-iron from the Bernberg: *a.* Grey;—*b.* Ordinary white;—*c.* Very light white;—*d.* White, and of normal composition;—*e.* Perfectly bright or specular iron containing 7 per cent. of manganese. (Bromeis, *Ann. Pharm.* 43, 241.) All the numbers refer to 100 parts.

	Karsten.				
	a.	*b.*	*c.*	*d.*	*e.*
Combined Carbon	0·89	1·03	0·75	0·58	0·95
Free Carbon	3·71	3·62	3·15	2·57	2·70
Total	4·60	4·65	3·90	3·15	3·65

	Bromeis.				
	a.	*b.*	*c.*	*d.*	*e.*
Combined Carbon	0·93	1·514	2·518	2·908	3·10
Free Carbon	2·34	1·040	0·500	0·550	0·72
Total	3·27	2·554	3·018	3·458	3·82

Bright iron contains the largest proportion of carbon, viz. 5·3 per cent=Fe^4C. [This is contradicted by the above analysis of Bromeis.] This quantity of carbon is not increased by fusion in a crucible lined with charcoal. With 4·25 per cent. of carbon, the laminar texture is still distinct; with a smaller quantity of carbon, it passes into the radiated; with a still smaller quantity, it exhibits a close and then a granular fracture, the whiteness at the same time diminishing; but when the proportion of carbon is still further diminished, the grey colour becomes lighter again. *Porous* cast-iron contains 3·5 per cent. carbon. (Karsten.)

The substances which occur in pig-iron in addition to the carbon, probably form compounds with a portion of the iron, which are finely diffused through or dissolved in the carbide of iron. These admixtures affect the quality of the iron as follows:—

Phosphorus imparts to iron the property of fusing tranquilly, and forming a thin liquid; and since phosphide of iron solidifies less quickly than pure iron, it is well adapted for castings; but if the proportion of phosphorus amounts to 1·5 per cent., the iron loses its solidity. The largest proportion of phosphorus, as it occurs in iron from Limonite, amounts to 5·6 per cent. (Karsten.) ¶ Schafhäutl (*J. pr. Chem.* 40, 304) remarks that cast-iron, bar-iron, and steel almost always contain more or less arsenic and phosphorus, which often greatly improve their quality. Thus the celebrated Dannemora iron and the English Low-Moor iron owe their good qualities to the presence of arsenic; and a particular kind of Russian iron (marked CCND) from Demidorff's works at Nischnetagilsk is indebted for its peculiar qualities to the phosphorus which it contains. ¶

Iron which contains *sulphur* becomes viscid and solidifies quickly, if cooled in the least degree after fusion, and during the solidification,

cavities and air-bubbles are often formed. Even if the quantity of sulphur amounts to only 0·37 per cent., the metal when converted into bar-iron is perfectly useless, breaking to pieces under the hammer at a red heat.—When a small quantity of sulphur ($\frac{1}{5}$ to $\frac{1}{8}$) is stirred about at the bottom of melted grey pig-iron prepared from manganiferous brown iron-stone, the fused mass solidifies in the form of *bright* iron, exactly resembling that from which rough steel is prepared. Pig-iron free from manganese likewise, when thus treated, yields bright iron, containing: Fe 94·03,—combined carbon 4·95 (it does not contain graphite),—S 0·61, —Si 1·05 (excess 0·62.) Even if this process does not produce bright or specular iron, it at least always yields white iron. On the other hand, fused bright iron obtained from spathic iron-ore is, by admixture of sulphur, completely converted into grey pig-iron. In all these fusions with sulphur, a black mass consisting of graphite and sulphide of iron separates on the surface of the metal. [Consequently, the sulphur expels a portion of the carbon from its combination with the iron.] (Huene, *J. pr. Chem.* 26, 308.)

Silicium becomes mixed with the iron in considerable quantity when coke is used as the reducing agent; the largest amount found by Karsten was 3·46 per cent. A larger proportion deprives grey cast-iron of its lustre, and gives it a dull aspect and an ash-grey colour; a similar effect is produced by other *earth-metals.* Generally speaking, grey cast-iron contains more silicium and manganese than the white variety. (Karsten.)

Arsenic occurs in pig-iron more frequently than is commonly supposed. It is not evolved in the form of arseniuretted hydrogen gas when the iron is dissolved in dilute sulphuric acid, but remains in the black residue, from which it may easily be extracted by caustic potash or hydrosulphate of ammonia, and then precipitated by acids in the form of sulphide of arsenic, or, in the case of the potash-solution, by passing sulphuretted hydrogen through the liquid, and boiling. This sulphide of arsenic often leaves a small quantity of sulphide of molybdenum when distilled. (Wöhler, *Ann. Pharm*, 31, 95.)

Sefström reduced ferric oxide mixed with various foreign substances, in a charcoal crucible before the blowpipe, whereby different elements, such as phosphorus, sulphur, arsenic, silicium, calcium, magnesium, aluminum, and manganese were made to combine with the iron, and alter its properties. (For the results of these important experiments, vid. *J. techn. Chem.* 10, 145.)

Cast-iron, when heated in the air, exhibits the same surface-colours as steel and bar-iron. White iron shows colour sooner than steel; cast-iron sometimes more slowly than bar-iron. (Karsten.) Cast-iron, by continued ignition in the air, is converted from without inwards into scale-oxide, the carbon at the same time escaping.—If the ignition be interrupted before the white cast-iron is completely converted into scale-oxide, the remaining iron, from loss of carbon, is found to be dark-grey, soft and malleable like the softest grey cast-iron, but does not appear brittle or porous. If it be protected from the air during ignition by covering it with various powders, even with charcoal powder, it is converted into the same kind of soft cast-iron, without much formation of scale-oxide. The same conversion takes place without any formation of oxide, when white cast-iron is surrounded with chalk, ashes, or ferric oxide, and ignited in close vessels. On this property depends the *annealing* of iron castings.—Grey cast-iron when exposed to the air covers itself with scale-oxide, and at

the same time becomes more and more brittle till it is completely oxidized. It likewise passes into a brittle, porous state, when heated to redness under chalk, ferric oxide, &c.—If white cast-iron is heated in the air till it becomes soft and pasty, it gives up its carbon more quickly than when merely heated to redness, and ultimately passes from the steel-like state to that of pure iron, without the great loss of iron which is unavoidable when the metal is completely fused. Since, however, when the amount of carbon is considerable, the pasty condition quickly passes into the liquid state, this mode of removing the carbon cannot be applied to bright iron, which is very rich in that element.—White or grey cast-iron, when fused in the air, becomes covered with scale-oxide, and if this be constantly removed, the whole of the metal is quickly oxidized; if, however, the oxide be left on the surface, it increases but slowly, and the iron becomes more free from carbon, more like steel, and difficult to fuse. —Grey cast-iron fused under a layer of carbonate of potash, soda, lime, or magnesia, the temperature being raised as the metal becomes more refractory, is converted into perfectly malleable steel-like iron. It cannot, however, be completely deprived of carbon by this process; neither does it take up any alkali-metal. The carbonic acid in the carbonates is doubtless converted into carbonic oxide. (Karsten.)

Nitric acid forms a black spot upon cast-iron, dissolves it with evolution of nitrous gas and carbonic acid, and leaves a brown, soft, mouldy residue. This latter substance smells like peat when heated, and glows when set on fire, emitting the same odour and leaving a greyish-red ash. Many kinds of this mouldy substance are slightly soluble in water, others more abundantly, especially in hot water, from which they separate partly by cooling, partly by evaporation; but all varieties of it dissolve easily in ammonia and potash, forming a black-brown solution, from which acids throw down a precipitate. (Berzelius, *Scher. Ann.* 7, 224.) If cast-iron be immersed in water, and nitric acid free from nitrous and hydrochloric acid be gradually added so that the temperature may not rise above 50°, there remains a black-brown mould, which, when heated in the air, emits fumes of a peculiar but not exactly empyreumatic odour, and then burns away with a glimmering light; when subjected to destructive distillation, it leaves a residue of charcoal, and yields a distillate of ammonia, together with an empyreumatic oil which smells like tobacco. (Berzelius, *Pogg.* 27, 126.)—Cold nitric acid of specific gravity 1·3 gradually dissolves white cast-iron, with separation of black flakes, which if left immersed in the acid, slowly acquire a brown-red colour; boiling nitric acid or aqua-regia acts in the same manner, but more quickly and with great frothing.—On grey cast-iron, cold nitric acid acts but slowly; the softer kinds are affected by the acid in the same manner as soft steel—the harder and lighter varieties (*e. g.* the mottled), like hard steel. After a time the action ceases altogether, but begins again if the graphite-laminæ are separated from the iron. Nitric acid is coloured by the mould which it dissolves. Aqua-regia acts in the same manner as nitric acid. (Karsten.)

Dilute sulphuric or hydrochloric acid also dissolves cast-iron—the grey more easily than the white—with evolution of hydrogen gas, contaminated with the vapour of a disagreeably-smelling oil, sometimes also containing sulphur and phosphorus, and perhaps mixed with marsh-gas; a carbonaceous residue is left, exhibiting three varieties of composition and properties. If the hydrogen gas, as it is evolved, is passed through alcohol, that liquid takes up the oil (first observed by Proust [*Scher. J.*

9, 480; also *Gilb.* 24, 293]), which may then be separated from it by adding water. When cast-iron is dissolved in hydrochloric acid, more hydrogen and less oil are obtained than when sulphuric acid is used; part of the oil remains in the carbonaceous residue, and may be extracted by alcohol. (Berzelius.) Oil of vitriol through which the hydrogen is passed, completely absorbs the vapour of the oil, acquiring a yellow and afterwards a deep-red colour. (Schrötter, *Ann. Pharm.* 39, 302.)—When cast-iron is dissolved in hydrochloric acid, there remains a brownish residue, which turns light yellow on drying, and when burnt becomes black, and leaves a residue of silica. Sulphuric acid leaves a black and more copious residue, which also leaves silica when burnt. (Berzelius.) —White cast-iron is almost insoluble in dilute sulphuric or hydrochloric acid; when immersed for some weeks in either of these acids, it becomes covered with a black dust or mould. Stronger sulphuric acid at a boiling heat dissolves white iron, leaving a residue of black carbonaceous matter having a metallic aspect [mould ?]; boiling concentrated hydrochloric acid dissolves white iron completely.—Grey cast-iron dissolves very slowly in dilute sulphuric or hydrochloric acid, and after a few months, leaves a residue consisting of three different substances : 1. Graphite, in non-magnetic scales, which have a metallic lustre, are insoluble in acids and alkalis, and burn without residue. 2. A magnetic, graphite-like mass (FeC^3) which becomes heated when dried in the air, and is in other respects similar to that which is obtained by the same process from unhardened steel (p. 210). 3. Black-brown, non-magnetic mould, which burns away below a red heat, and dissolves in caustic potash, forming a black-brown solution. Graphite is never absent from the residue; but it is mixed, sometimes with the graphite-like matter, sometimes with mould. When grey cast-iron is dissolved in strong sulphuric acid, the residue consists of graphite, and black, easily inflammable mould; hot concentrated hydrochloric acid dissolves grey iron quickly, leaving a residue of graphite.—White cast-iron which has been rendered grey and soft by continued ignition, comports itself with nitric, sulphuric, and hydrochloric acid in the same manner as unhardened steel which has been rendered denser by hammering. (Karsten.)—¶ Acccording to Landrock (*Arch. Pharm* [2], 54, 1), the insoluble residue left by the action of dilute sulphuric acid on cast-iron does not in any way partake of the nature of an organic substance; and that which is dissolved out of it by potash is not a substance resembling mould or humus, but consists mainly of ferric oxide and silica, the ferric oxide being rendered soluble in potash through the medium of the silica; the volatile products resulting from the action of the acid are hydrogen, arseniuretted, phosphuretted, and sulphuretted hydrogen, and sulphurous acid ¶.—When the residue obtained on dissolving grey cast-iron in hydrochloric acid is treated with ammonia, it rapidly gives off hydrogen, together with traces of marsh-gas, and yields alumina (so far as all kinds of cast-iron contain aluminum) and silica to the ammonia. The residue left on dissolving white iron in hydrochloric acid, does not effervesce with ammonia, provided no grey-iron was mixed with the white. (Schafhäutl, *briefliche Mittheilung.*) ¶ According to Hull (*Ann Pharm.* 74, 112), the evolution of hydrogen in the manner just mentioned is purely a mechanical phenomenon. The hydrogen is, in fact, mechanically inclosed in the porous carbonaceous residue, and is evolved from it, not only by contact with ammonia, but likewise by boiling with pure water. Its liberation by ammonia at ordinary temperatures, probably arises from this circumstance, that the ammonia dis-

solves the oily hydrocarbon contained in the carbonaceous residue, thereby wetting and penetrating it completely ¶.

Daniell (*Schw.* 19, 202) by dissolving cast-iron in hydrochloric or sulphuric acid, obtained a substance which could be cut with the knife, and when dried in the air upon blotting-paper, became heated, and, if in mass, even took fire spontaneously.—Cannon-balls (not all) which had lain for 42 years under sea-water, were found to be converted into a substance like plumbago, some to the thickness of half an inch, others to the very centre. (Silliman, *Sill, Amer. J.* 4, 178; also *Schw.* 35, 481.) [The balls which withstood the action of the sea-water probably consisted of white cast-iron.]—Cannon-balls lying in the sea on the coast of Normandy, where they had been deposited during a sea-fight in 1692, had retained their form and bulk, but lost two-thirds of their weight; they yielded to the knife, had no action on the magnet, and no longer contained metallic iron. (Deslongchamps, *J. Chim. Méd.* 13, 89.) Balls raised at Carlscrona from a ship sunk 50 years before, were found to be converted, through one-third of their mass, into a porous, graphitic substance, which became strongly heated when exposed to the air for a quarter of an hour, so that the adhering water evaporated. (Berzelius, *Lehrb.*)—Sea-water does not extract all the iron from cast-iron, but, like dilute sulphuric acid, leaves graphite mixed with a graphitic substance (FeC^3) which, as it dries in the air, becomes heated even to redness. Cast-iron immersed in fresh-water is likewise converted by the carbonic acid of the air—though very slowly and with deposition of iron-rust—into the same mixture of graphite and FeC^3. (Karsten.) Oxidation of cast-iron—even more rapid than in sea-water—likewise takes places at the mouths of rivers falling into the sea, where, at the ebb and flow of the tide, the lower part of the iron is placed in contact with sea-water, and the upper part with river-water, so that a galvanic [Bucholzian] circuit is formed. Foul sea-water acts more strongly, in consequence of the hydrosulphuric acid which it contains. The surface of the iron, which, by the sudden cooling in moist sand, has been brought to a state approaching more nearly to that of white cast-iron—resists the action of the water better than the interior. (Mallet, *J. pr. Chem.* 22, 352.)—Aqueous chloride of copper extracts all the iron from cast-iron, leaving behind the whole of the carbon mixed with copper. (Berzelius, *Pogg.* 46, 42.)—A similar action is produced when cast-iron is placed in contact with a lump of fused chloride of silver under water containing a few drops of hydrochloric acid. The silver is thereby reduced. (Berzelius.)—The harder kinds of white cast-iron placed in contact with water and chloride of silver are slowly decomposed, leaving a black-brown mould; the softer kinds decompose more quickly and leave graphite, black-brown mould, and the graphitic mass FeC^3, which, by longer action of the chloride of silver, is likewise converted into black-brown mould, though less quickly than in dilute acids. Grey cast-iron gives with water and chloride of silver a mixture of graphite and FeC^3. (Karsten.)—Aqueous solution of iodine acts in the same manner as the metallic chlorides. (Berzelius.)

White or grey cast-iron immersed in charcoal powder and ignited for a long time, or fused, takes up from 1 to 1½ per cent. more carbon, unless it is previously saturated with carbon like bright iron, and the white variety, when heated to redness between charcoal, becomes grey and soft. (Karsten.)

[Upon bar-iron, steel, and cast-iron, see especially Karsten (*System der Metallurgie*, 1831–32, Bd. 4; also *Schw.* 66, 51 and 166). The numerous experiments of

Scharfhäutl (*J. pr. Chem.* 19, 150 and 408; 20, 465; 21, 129) are also well worthy of notice.]

d. Pure, Saturated Cast-iron.—Fe^4C.—By fusing finely divided iron or steel with charcoal once or more, a dark grey, fusible carbide of iron is obtained, having a laminar texture, and capable of being pounded in a mortar. (Faraday & Stodart, *Gilb.* 66, 183.) Bar-steel fuses to a similar compound, if the cementation be carried too far. (Buttery.) The carbide of iron obtained by continued cementation of iron with lamp-black, resembles ordinary cast-iron in the appearances which it presents at a red or a melting heat, and in its reactions with other bodies. (Karsten.) 4 atoms of iron strongly ignited or fused with excess of charcoal appear to take up at most 1 atom of carbon.

					Faraday & Stodart.
4Fe	108	....	94·73	.....	94·36
C	6	....	5·27	.....	5·64
Fe^4C	114	....	100·00	.....	100·00

e. Fe^2C^3.—When Prussian blue is ignited in close vessels, there remains a black powder, which, if exposed to the air while still warm, takes fire and burns away, yielding carbonic acid and sesquioxide of iron. (Proust, Ittner, Berzelius.) Robiquet regards the residue as a mere mixture, since it is magnetic, rusts by contact with water, and readily gives up its iron to hydrochloric or sulphuric acid, with evolution of hydrogen.

f. FeC^2.—Ferrocyanic acid or ferrocyanide of ammonium heated in a close vessel, leaves bicarbide of iron, which, when strongly heated in nitrogen gas exhibits, a glimmering light unattended with chemical change. It is a loose, black powder, which, when slightly heated in the air, burns like tinder and is converted into ferric oxide of equal weight. (Berzelius.)

g. FeC^3 ?—Sometimes left behind, together with graphite, in the action of dilute sulphuric or hydrochloric acid, sea-water, &c., on unhardened steel and grey cast-iron; it forms a graphite-like but magnetic mass, which oxidizes in the air with considerable evolution of heat, is converted into mould by the continued action of acids, and when burnt, leaves from 82 to 94 per cent. of ferric-oxide. (Karsten; *comp.* pp. 204, 205, 209, 218).—Berthier (*Jahresber.* 14, 130) obtained a similar mass by treating cast-steel with aqueous bromine or iodine in quantity not sufficient to dissolve the whole of the iron; it was in the form of the iron, could be pressed between the fingers, and was magnetic; it was not decomposed by excess of bromine or iodine, until all the free iron was dissolved. It contained 81·7 per cent. iron and 18·3 carbon; hence its formula should be FeC.

B. Carbonate of Ferrous-oxide, or Ferrous Carbonate.—*a. Monobasic.*—The anhydrous occurs in the forms of *Iron-spar, Spathic Iron-ore, Stahlstein* or *Sphærosiderite*, and *Junkerite*. Iron-spar is isomorphous with calcspar. An acute rhombohedron, *Figs.* 141, 143, 145; $r' : r^3 = 72^\circ\ 58'$; $r^3 : r^5 = 107^\circ\ 2'$. Cleavage parallel to *r*. (Hauy.) Specific gravity 3·829 (Mohs), 3·872 (Neumann). Harder than calcspar; white and translucent. In iron-spar, part of the ferrous carbonate is often replaced by the isomorphous carbonates of lime, magnesia, and manganous oxide.—Junkerite forms yellowish-grey rectangular octohedrons. (*Fig.* 47.) Cleavage perpendicular to the axis and parallel

two diagonals (angles = 108° 26′ and 71° 34). Specific gravity 3·815. Harder than calcspar. It therefore exhibits with regard to iron-spar the same dimorphism that arragonite exhibits with regard to calcspar. (Dufrénoy, *Ann. Chim. Phys.* 56, 198; also *J. pr. Chem.* 3, 261.) According to Breithaupt (*Pogg.* 58, 278), on the contrary, junkerite has the same form as iron-spar, and the so-called octohedron which it exhibits arises from the truncation of an acute rhombohedron, *Fig.* 153.

Iron-spar when heated to redness gives off 4 volumes of carbonic acid gas and 1 volume of carbonic oxide, and leaves black magnetic ferroso-ferric oxide:

$$5FeO,CO^2 = 3FeO,Fe^2O^3 + 4CO^2 + CO.$$

(Döbereiner, *Schw.* 28, 43.) According to Fuchs, also (*J. pr. Chem.* 17, 168) the residue left after the ignition of iron-spar contains much more ferrous and less ferric oxide than magnetic iron-ore. ¶ According to Glasson (*Ann. Pharm.* 62, 89), iron-spar when ignited out of contact of air, gives off 5 volumes of carbonic acid to 1 volume of carbonic oxide, and the residual oxide consists of 4 FeO, Fe^2O^3. ¶ Hydrate of potash likewise converts iron-spar into ferroso-ferric oxide, abstracting the carbonic acid and liberating carbonic oxide, but only on the application of a considerable degree of heat. (Döbereiner.) In damp air, iron-spar is very slowly converted into hydrated sesquioxide of iron. When heated in a current of chlorine gas, it yields a sublimate of sesquichloride of iron and a residue of sesquioxide, mixed with protochloride if the quantity of chlorine is deficient:

$$6(FeO,CO^2) + 3Cl = 2Fe^2O^3 + Fe^2Cl^3 + 6CO^2.$$

(Wöhler, *Ann. Pharm.* 29, 253.) Hydrochloric acid dissolves iron-spar but slowly, with evolution of carbonic acid. The mineral does not dissolve in aqueous hydrochlorate or nitrate of ammonia. (Brett.)

FeO	35		61·404
CO^2	22		38·596
FeO,CO^2	57		100·000

The *hydrated salt* is precipitated, on mixing a ferrous salt with carbonate of potash or soda, in thick flakes, which, when exposed to the air, abstract oxygen and evolve carbonic acid, first assuming a dirty green colour, and then changing to yellowish-brown ferric hydrate.

It is very difficult in preparing this substance (for medical purposes) to wash and dry the precipitate without allowing it to undergo the change just mentioned, to a considerable extent.—The green vitriol used must be perfectly free from ferric sulphate, *e. g.*, that obtained by Bonsdorff's process,—and this salt, as well as the monocarbonate or bicarbonate of soda or potash used as the precipitant, must be dissolved in water perfectly freed from air by boiling. (Bicarbonate of potash gives a dense pulverulent precipitate: *G. Schmidt.*) The precipitation is performed as much as possible out of contact of air, with excess of the alkaline carbonate, and for the most part in the cold. Wilkens and Wittstein, however, recommend precipitation at a boiling heat, followed by a quarter of an hour's boiling, whereby the flocculent precipitate collects into a powder which is easier to wash. If, however, the liquid contains a large quantity of carbonate of soda, the precipitate turns *greyish-black* on boiling. (Geiger.) It is washed with boiling water

either on a cloth filter, with frequent agitation and straining, and lastly pressed between bricks (Bolle); or, by Schindler's method, in a bottle with the bottom cut off and bound round with linen, and having a long tube filled with boiled water adapted to its mouth, as in Real's press (Wilkens); or it is washed by decantation in a stoppered bottle kept constantly full of water freed from air by boiling.—The precipitate, after thorough washing, is either quickly introduced into a bag of bibulous paper, and the whole tied closely up in a moist bladder and dried between 50° and 60° (Wilkens); or inclosed in a bladder without the paper (Daum). Or the precipitate, after thorough washing by decantation, is agitated with alcohol instead of water, the liquid decanted, and the wet mass introduced into a tubulated retort, previously connected air-tight with a receiver which has been exhausted of air as completely as possible by burning alcohol in it. The tubulus of the retort having been stopped and a gentle heat applied, the alcohol passes over and the residue becomes dry. If too strong a heat be applied, the carbonic acid escapes. (Fölix.) Or the moist precipitate, after having been covered with ether in a retort, is dried at a gentle heat in a distillatory apparatus filled with ether vapour (p. 171), after which dry carbonic acid gas is then made to pass through the apparatus; by this treatment, the precipitate is rendered somewhat less liable to change by exposure to the air. (G. Schmidt.)

The preparation, when tolerably successful, is a greenish-white or dark green, rather heavy, finely divided, and tasteless powder, containing from 24 to 30 per cent. of carbonic acid. When ignited out of contact of air, it yields water, carbonic acid and carbonic oxide, and leaves magnetic ferroso-ferric oxide, which, after cooling in air-tight vessels, takes fire on exposure to the air. The moist powder becomes perfectly dry after exposure to the air for some days, giving off carbonic acid and being completely converted into ferric oxide. When not well dried, it oxidizes quickly in the air, becoming very hot and giving off vapour of water. But if mixed with sugar while in the moist state, it acquires a coating of syrup which renders it more permanent. (Klauer.) When treated with hydrochloric acid, it rapidly evolves carbonic acid. (*Comp.* J. A. Buchner, Daum, L. A. Buchner, Wittstein, F. W. Schmid, *Repert.* 16, 235; 41, 279 and 285; 61, 210; 67, 270; Bolle, *Berl. Jahrb.* 33, 1, 124; Fölix, *Br. Arch.* 38, 149; Wilkens, Klauer, *Ann. Pharm.* 10, 86; 19, 129; Vallet, *J. Pharm.* 24, 289.)

b. Acid salt, Aqueous solution.—Formed by dissolving the normal salt —or metallic iron, which dissolves with evolution of hydrogen—in aqueous carbonic acid, out of contact of air. The colourless solution, which has a slightly ferruginous taste, is decomposed with precipitation of hydrated ferric oxide, if the air has access to it even but sparingly; it yields a black precipitate with hydrosulphuric acid, and, according to Pfaff, a purple precipitate with tincture of galls. According to Vauquelin (*J. Pharm.* 13, 266), the black precipitate with hydrosulphuric acid is not produced till the solution has been exposed to the air for some time; it then forms as the carbonic acid escapes. To preserve chalybeate water in vessels, they must first be filled with carbonic acid gas, then filled below the surface of water with the chalybeate, and lastly corked under water. A less efficient mode of preservation is the introduction of iron-wire or of 4 grains of sugar. In sugared chalybeate water, hydrosulphuric acid and sulphide of iron may be detected after the water has been kept for a year. (Bischof, *Schw.* 57, 26; *J. pr. Chem.* 1, 341.)

C. *Ferric Carbonate?*—The precipitate thrown down by alkaline carbonates from ferrous salts, contains, after thorough washing and exposure in thin layers to the moist air of a cellar for half-a-year, 71·4 per cent. of ferric oxide (perfectly free from ferrous oxide), 8·3 carbonic acid, and 20·0 water. (Soubeiran, *Ann. Chim. Phys.* 44, 326; also *J. Pharm.* 16, 524.)—The precipitate formed by mixing carbonate of potash with nitrate of ferric oxide consists, after proper washing with cold water, of hydrated ferric oxide, perfectly free from carbonic acid. (Gm.)

Iron and Boron.

According to Arfvedson's experiments, no such compound as *Boride of Iron* appears to exist (vid. II., 100). The so-called boride of iron which Lassaigne (*J. Chim. Méd.* 3, 535) obtained by igniting borate of ferric oxide in a current of hydrogen was probably a mere mixture of iron and boracic acid. (Gm.)

A. Borate of Ferrous Oxide, or Ferrous Borate.—Borax added to solution of ferrous sulphate throws down a pale yellow powder, which melts before the blowpipe to a bead (Scheele), and from which a large quantity of acid may be extracted by water. According to Tünnermann (*Kastn. Arch.* 20, 21), the precipitate is greyish-green, and gives up all its acid when washed.

B. Borate of Ferric Oxide, or Ferric Borate.—Yellowish powder insoluble in water: when heated, it turns brown and afterwards fuses to a glass. (Berzelius, *Lehrb.*)

Iron and Phosphorus.

A. Phosphide of Iron.—*a.* Fe^4P.—Found by Bergman (*Opusc.* 3, 109) and Meyer in cold-short iron, and regarded as a peculiar metal, for which the name *Siderum* or *Hydrosiderum* was proposed: it was afterwards recognized as phosphide of iron by Meyer, Klaproth, and Scheele. —1. Prepared by passing phosphorus vapour over red-hot iron filings, or throwing pieces of phosphorus upon them. (Hatchett.)—2. By igniting iron filings with an equal weight of glacial phosphoric acid, either with or without $\frac{1}{10}$ part of charcoal dust. (Pelletier.) Or by exposing 8 parts of iron filings, 10 bone-earth, 5 fine quartz-sand, and 1 charcoal-powder to a heat sufficient to melt the silicate of lime. (Wöhler.)—3. By igniting phosphate of ferrous oxide with $\frac{1}{4}$ its weight of lamp-black. With a larger quantity of lamp-black, a mixture of phosphide and carbide of iron is obtained (the latter may be dissolved out by hydrochloric acid); but half of the phosphorus always volatilizes during the operation. (Berzelius.)

Colour dark steel-grey (H. Davy); white, streaked on the fractured surfaces (Hatchett). Pulverizable; specific gravity 6·7. According to Hatchett, it is magnetic and may be made polar. According to Berzelius, on the contrary, it is non-magnetic; hard and susceptible of polish; brittle, with granular fracture; sometimes crystallizes in prisms after fusion; fuses much more easily than cast-iron.

			Berzelius (3.)	Pelletier (2.)
4Fe	108·0	77·47	76·805	80
P	31·4	22·53	23·195	20
Fe^4P	139·4	100·00	100·000	100

When fused before the blowpipe, it slowly becomes covered with a black slag of phosphate of iron, and gives up its phosphorus but slowly, even in the inner flame. Not attacked by cold hydrochloric, sulphuric, nitric, or nitro-hydrochloric acid. Dissolves but slowly in strong nitric or nitro-hydrochloric acid: the former solution, if formed from 4 parts of phosphide of iron, leaves on evaporation 6·5 parts of ferric phosphate. (*Berzelius.*)

b. Two-thirds Phosphide.—Fe^3P^2.—Formed by passing phosphuretted hydrogen gas over gently heated iron pyrites:

$$3FeS^2 + 2PH^3 = Fe^3P^2 + 6HS.$$

The pulverulent compound gives a phosphorus flame before the blowpipe. It dissolves in nitric acid and aqua-regia; but not in hydrochloric acid even when concentrated. (H. Rose, *Pogg.* 24, 333.)

				H. Rose.
3Fe	81·0	56·33	56·87	54·92
2P	62·8	43·67	43·13	45·08
Fe^3P^2	143·8	100·00	100·00	100·00

B. Hypophosphite of Ferrous Oxide, or Ferrous Hypophosphite.—Iron dissolves in aqueous hypophosphorous acid out of contact of air, with evolution of hydrogen gas. The solution evaporated in vacuo yields a light green, crystalline mass which when heated in a retort behaves like the zinc-salt. (H. Rose, *Pogg.* 12, 294.)

C. Hypophosphite of Ferric Oxide, or Ferric Hypophosphite.—Hydrated ferric oxide dissolves sparingly in the cold acid; but without reduction to the state of ferrous oxide, and forms a white salt which is difficultly soluble in the free acid, and when heated gives off easily inflammable phosphuretted hydrogen. On boiling the hydrated oxide with the acid, a solution of ferrous hypophosphite is obtained, while ferric phosphate is precipitated.

D. Phosphite of Ferrous Oxide, or Ferrous Phosphite.—Formed by precipitating green vitriol with terchloride of phosphorus dissolved in water and neutralized by ammonia—washing the precipitate, which is white, but soon acquires a slight greenish colour, with boiling water—and drying it in vacuo. During this treatment, the superficial portions become oxidized and converted into brown-red basic phosphate of ferric oxide. The filtrate, when kept in a close vessel, deposits a small additional quantity of the salt, and then becomes slightly turbid on boiling.—The dried salt, when ignited in a retort, gives off pure hydrogen gas with incandescence and leaves diphosphate of ferrous oxide. The residue contains (besides 0·12 p. c. of a black phosphorous-compound insoluble in hydrochloric acid) 53·65 per cent. of ferrous oxide and 46·35 phosphoric acid. (H. Rose, *Pogg.* 9, 35.)

E. Phosphite of Ferric Oxide, or Ferric Phosphite.—Terchloride of phosphorus mixed with water and ammonia yields with double sulphate of ferric oxide and ammonia, a white precipitate soluble in excess of the iron-salt; this precipitate must be washed with cold water and dried in vacuo. The liquid filtered from the precipitate deposits, after long standing, a large additional quantity of the salt, of a white

colour.—The white salt when heated to redness in a retort, exhibits a glimmering light, gives off hydrogen gas—which contains phosphorus and therefore gives a precipitate with silver-solution, but does not take fire spontaneously in the air—and leaves a white residue dotted with black specks. These spots are due to the presence of a small quantity of a black phosphorus-compound amounting to 0·9 per cent.; the hydrochloric acid solution of the residue yields a quantity of ferric oxide amounting to 52·46 per cent. of that residue, in which, however, it existed partly in the state of ferrous oxide. (H. Rose.)

F. Phosphate of Ferrous Oxide, or Ferrous Phosphate.—*a. Terbasic.*—Found in the hydrated state, as *Blue Iron-ore* or *Vivianite.*—Crystalline system, the oblique prismatic. *Fig.* 81, 82, and other forms. $u' : u = 111° 6'$; $i : m = 125° 18'$; Sp. gr. 2·6. Softer than calcspar. Indigo-blue, producing a light blue powder; transparent, with a pearly lustre. Fuses very readily before the blowpipe, with intumescence and loss of water, forming a grey, shining, magnetic bead, and imparting a bluish-green colour to the flame. Boiling potash-solution extracts phosphoric acid from it and turns it black. Easily soluble in hydrochloric or nitric acid.

Earthy Phosphate of Iron, or *Blue Iron-earth*, appears likewise to belong to this head; as this mineral is often white when first dug up and afterwards turns blue on exposure to the air, it is probable that the blue colouring is due to the presence of a certain quantity of ferric phosphate.

$3FeO, cPO^5 + 8Aq.$		*a.*	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
$3FeO$	105·0	42·27	41·23	41·0	45	42·65	48·79	42	43·0
PO^5	71·4	28·75	31·18	26·4	21	24·00		28	23·1
$8HO$	72·0	28·98	27·48	31·0	34	25·00	26·26	26	32·4
					Sand 7·90		Mould 4		
						Al^2O^3, 0·6;	—Mn^2O^3, 0·3		0·9
	248·4	100·00	99·89	98·4	100	99·55		100	99·4

a. Vivianite from St. Agnes in Cornwall, according to Stromeyer.—*b.* From Bodenmais, according to A. Vogel.—*c.* From the Isle of France, according to Fourcroy & Laugier.—*d.* From the Mullica Hills, New Jersey (the so-called *Mullicite*), according to Thomson.—*e.* From Kertsch, in the Crimea, according to Segeth.—*f. Blue Iron-earth* from the Hagenbruch, near Brunswick, according to Wiegemann.—*g. Blue Iron-earth* from Alleyras, according to Berthier.

A pit in a town had been filled for centuries with heaps of bones, wood, gneiss, &c. On the carbonized pieces of wood, and likewise on the micaceous laminæ of the gneiss (which contained iron), but not on the other constituents of it, were seen white crystals of ferrous phosphate which turned blue on exposure to the air.—Iron plates immersed in aqueous phosphate of ammonia become covered with white crystalline ferrous phosphate.—If the arm *a* of the bent tube (*App.* 4) contains solution of blue vitriol, together with a copper rod, the arm *b* containing phosphate of soda with an iron rod, and if the two liquids are separated at *h* by moist clay, and the iron is placed in connexion with the copper, white crystalline nodules, which quickly assume a fine blue colour on exposure to the air, are formed upon the iron. (Becquerel, *Ann. Chim. Phys.* 54, 149.)—¶ Some iron nails found in the stomach of an ostrich and partly enveloped in black animal matter, became covered, after several days'

exposure to the air, with blue spots, which appeared to arise from the formation of triphosphate of ferrous oxide (*Vivianite*). (Schlossberger, *Ann. Ch. Pharm.* 62, 382.) Hardinger (*J. pr. Chem.* 44, 81) mentions the occurrence of crystallized Vivianite in the hollow of a bone in the skeleton of a miner found in an old working at Tarnowitz. ¶

b. Bibasic ?—Ordinary diphosphate of soda gives a white precipitate with ferrous salts. The precipitate acquires a dirty bluish-green colour on exposure to the air. It fuses readily before the blowpipe, and solidifies in a crystalline mass on cooling: it is not reduced to the state of phosphide of iron when heated on charcoal alone, but only on the addition of carbonate of soda. (Berzelius.) It is insoluble in water and in ammoniacal salts, but dissolves in aqueous acids and in ammonia. The solution in ammonia is of a dingy-yellow colour; and when exposed to the air, exhibits first a greenish, and then a brownish turbidity.

c. Acid Phosphate.—Aqueous phosphoric acid dissolves iron with evolution of hydrogen gas, forming an acid salt at first, but afterwards the more neutral salt is deposited in the form of a greyish-white substance. (Scheele.) The solution yields, with ammonia, a greenish precipitate, soluble in excess of ammonia. (A. Vogel.)

¶ G. Pyrophosphate of Ferrous Oxide, or Ferrous Pyrophosphate.—A ferrous salt mixed with pyrophosphate of soda yields a white, amorphous precipitate, which, when exposed to the air, immediately turns green, and afterwards brown. (Schwarzenberg, *Ann. Pharm.* 65, 153.) ¶

H. Phosphate of Ferric Oxide, or Ferric Phosphate.—*a. Polybasic.*—Remains in the form of a red-brown, somewhat fusible powder, when the sesquiphosphate is boiled with caustic potash. (Fourcroy & Vauquelin.)

Limonite, Bog Iron-ore (*Raseneisenstein, Sumpferz, Wiesenerz*).—Brown, with conchoidal fracture, fusing at the edges before the blowpipe. A mixture of bibasic(?) phosphate of ferric oxide, silicate of ferric oxide, humus-like ferric oxide, hydrated ferric oxide, quartz-sand, &c. in variable proportions. The quantity of phosphoric acid in it varies from 1·8 to 11 per cent.

b. Bibasic.—*α.* Ore from the Dpt. de la Haute Vienne. Brown needles arranged in radiated masses, producing an olive-green powder, and fusing before the blowpipe to a black opaque glass. (Vauquelin, *Ann. Chim. Phys.* 30, 202.) Of similar nature is *Green Iron-stone.* (Karsten, in his *Archiv.* 15, 243.)

					Vauquelin.		Karsten.
$2Fe^2O^3$	156·0	....	61·32	.....	56·20	....	63·45
MnO		....		.....	6·76		
PO^5	71·4	....	28·07	.....	27·84	....	27·72
3HO	27·0	....	10·61	.....	9·20	....	8·56
$2Fe^2O^3, PO^5 + 3Aq.$	254·4	....	100·00	.....	100·00	....	99·73

β. Ore from Berneau, in the district of Liege. Kidney-shaped, with a conchoidal, waxy fracture. Sp. gr. 1·85. Blackish, reddish, or yellowish brown; yields a brownish-yellow powder. Translucent at the edges. Decrepitates before the blowpipe, and yields a greenish-yellow bead. Falls to pieces in water; easily soluble in dilute hydrochloric acid. (Delvaux, *Bull. de l'Acad. de Bruxelles*, 1838, 147; Dumas, *Pogg.* 47, 496.)

In the analyses, an admixture of 10 or 11 per cent. of carbonate of lime and between 0·5 and 3·6 of silica has been deducted.

	Approximate Calculation.			Delvaux.	Dumont. Black-brown.	Dumont. Red-brown.
$2Fe^2O^3$	156·0	38·29		40·44	36·62	34·19
PO^5	71·4	17·53		18·20	16·57	16·04
20HO	180·0	44·18		41·13	46·81	49·77
$2Fe^2O^3,PO^5+20Aq.$	407·4	100·00		99·77	100·00	100·00

Beraunite, which crystallizes in ill-defined rhombic prisms, contains a tolerably large quantity of water, together with ferric phosphate free from ferrous oxide. Sp. gr. 2·878. Colour, hyacinth-red; translucent, with a pearly lustre. Fuses readily before the blowpipe, and dissolves easily in hydrochloric acid, leaving only a trace of silica. (Breithaupt & Plattner, *J. pr. Chem.* 20, 66.)

On *Karphosiderite*, vid. Breithaupt. (*Schw.* 50, 314.)

Melanchlore from Rabenstein, which has a density of 3·38, fuses readily before the blowpipe into a black magnetic bead, and is easily soluble in warm hydrochloric acid. Contains, besides impurities, about 3·87 per cent. of ferrous oxide, 38·9 ferric oxide, and from 25·5 to 30·3 phosphoric acid. (Fuchs, *J. pr. Chem.* 17, 171.)

c. *Sesquiphosphate.*—By precipitating sesquichloride of iron with ordinary diphosphate of soda:

$$2Fe^2Cl^3+3(2NaO,cPO^5)=2Fe^2O^3,3cPO^5+6NaCl.$$

This calculation, however, is not in accordance with A. Vogel's analysis, which gives 37 per cent. ferric oxide, 38 acid, and 24 water. The white flocculent precipitate retains its colour when dry; but at a red-heat it gives off water, turns yellow, and afterwards fuses to a grey bead. (Bergman, *Opusc.* 3, 118.) With carbonate of soda upon charcoal, it yields phosphide of iron. (Berzelius.) Caustic potash immediately colours the precipitate red-brown, by withdrawing the greater part of its acid, but does not dissolve any ferric oxide. Ammonia exhibits the same reaction, provided no phosphate of soda is present in excess; in the latter case, the ammonia turns the precipitate brown and then dissolves it, forming a red-brown solution. The ammoniacal solution remains clear when mixed with ferrocyanide of potassium, but yields Prussian blue on the addition of an acid. (H. Rose, *Pogg.* 43, 587.) The salt can only be separated from the ammoniacal solution by evaporation. (Döbereiner, *Schw.* 26, 271.) Carbonate of ammonia likewise dissolves the precipitate. (Berzelius, *Pogg.* 27, 131.) When immersed in carbonate of soda, it slowly acquires a red-brown colour, and dissolves partially in a large excess of the liquid. (H. Rose.) The salt dissolves in 1500 parts of boiling water, and easily in dilute acids. (Bergman.) It does not dissolve in cold acetic acid, or in aqueous ammoniacal salts. (Wittstein, *Repert.* 63, 224.) The freshly precipitated salt dissolves slowly in warm aqueous sulphurous acid or sulphite of ammonia, the ferric oxide being reduced to the state of ferrous oxide. (Berthier.)

mon *Biphosphate?*—The solution of the salt c in aqueous phosphoric crystallizes kept for a year in close vessels, yields small, translucent, taste-to the au. having a vitreous lustre (sometimes with a pale rose-colour, 149.)—¶ Sou accidental presence of manganese). When heated, they enveloped in bla leave a dirty white, opaque mass, which, at a bright

red heat, fuses to a grey slag. They are insoluble in water, but dissolve in ammonia, forming a red solution, and very easily in hydrochloric acid, forming a light brown solution. (Winckler, *Repert.* 38, 197.)

	Approximate Calculation.		Winckler.
Fe^2O^3	78·0	26·63	25·0
$2PO^5$	142·8	48·77	52·5
8HO	72·0	24·60	22·5
$Fe^2O^3,2PO^5+8Aq.$	292·8	100·00	100·0

¶ I. Pyrophosphate of Ferric Oxide, or Ferric Pyrophosphate. —Obtained by dissolving sublimed sesquichloride of iron in water, and precipitating by phosphate of soda; the supernatant liquid is neutral. Nearly white powder, having a slight yellowish tinge, which deepens at 100°, and becomes lighter again after ignition. Dissolves in acids and in phosphate of soda, likewise in ammonia; in the latter it forms a yellow solution. Insoluble in hydrochloric acid, sulphurous acid, and sal-ammoniac. On dissolving it in hydrochloric acid without boiling, and precipitating by ammonia, the precipitate dissolves completely in excess of ammonia. Carbonate of ammonia dissolves it, forming a colourless solution, whereas the ordinary phosphate forms a yellow solution. It is completely decomposed by fusion with a mixture of carbonate of soda and carbonate of potash. The salt, after drying at 100°, lost by ignition 17·66 p. c. of water, and the ignited salt was found to contain 41·7 Fe^2O^3 + 58·3 PO^5. These numbers accord with the formula $2Fe^2O^3,3bPO^5$ + 9 Aq.

Acid sesquichloride of iron, precipitated by pyrophosphate of soda, yields, not pyrophosphate of ferric oxide, but an ordinary phosphate, containing 1 atom of base to 1 atom of acid; in 100 parts : 61·66 Fe^2O^3 + 48·34 PO^5. This salt, when boiled with ordinary phosphate of soda, does not yield pyrophosphate of soda, as is the case with the preceding. (Schwarzenberg, *Ann. Pharm.* 65, 153.)

K. Metaphosphate of Ferric Oxide, or Ferric Metaphosphate. —Formed by mixing sesquichloride of iron with excess of dilute phosphoric acid, evaporating to dryness, and heating the residue in a platinum capsule to 316°. White powder, insoluble in water and in dilute acids, but soluble in strong sulphuric acid. Contains 26·35 per cent. of Fe^2O^3, corresponding to the formula, $Fe^2O^3,3PO^5$. (Maddrell, *Ann. Pharm.* 61, 59.) ¶

Iron and Sulphur.

A. One-eighth Sulphide of Iron.—Formed by passing hydrogen gas over red-hot disulphate of ferric oxide; water is formed, sulphurous acid and a large quantity of hydrosulphuric acid given off,—and there remain 59·52 parts of sulphide of iron for every 100 parts of the dry salt used. Blackish-grey powder, producing a grey metallic streak. Contains 27 parts of iron to 2 pts. sulphur. When treated with dilute acids, it yields 7 volumes of hydrogen gas to 1 volume of sulphuretted hydrogen. (Arfvedson, *Pogg.* 1, 72.)

B. Disulphide of Iron.—100 parts of anhydrous sulphate of ferrous oxide, decomposed by hydrogen gas at a red heat, yield at first sulphurous acid and water, then hydrosulphuric acid, and leave 46·74 parts of disul-

phide of iron. Dark grey powder aggregated in lumps, strongly attracted by the magnet; contains 27 iron to 8 sulphur. Hydrosulphuric acid gas, passed over it at a red-heat, converts it into the sulphide of iron, corresponding to magnetic pyrites, whereby 35 parts are increased to 45. Dissolves in aqueous acids, with evolution of 4 vol. hydrogen gas to 1 vol. hydrosulphuric acid. When a mixture of 20 parts protosulphide of iron and 12 of iron wire is fused in a charcoal crucible, 2 layers are formed, the lower of which is cast-iron containing 2·5 per cent. of sulphur—from admixture of sulphide of iron—while the upper layer consists of protosulphide of iron mixed with a small quantity of cast-iron, often distinguishable by the eye. (Berthier, *Ann. Chim. Phys.* 22, 241.) Perhaps the presence of carbon hindered the formation of a lower sulphide; for, according to Berzelius, protosulphide of iron dissolves metallic iron at a strong heat, producing a lower sulphur-compound.

C. Protosulphide of Iron, or Ferrous Sulphide.—Occurs in small quantities in many meteorites; sometimes formed by the reducing action of putrefying organic bodies on ferrous sulphate contained in well-waters,—but under such circumstances it is always mixed with a higher sulphide. (Berzelius.) Heated iron-wire burns vividly in sulphur vapour (II, 221). A mixture of iron-filings and sulphur glows vividly when heated. Sulphur pressed against red-hot bar-iron (not cast-iron) perforates it by forming sulphide of iron. (Evain, *Ann. Chim. Phys.* 25, 106; also *Schw.* 43, 330.)—*Preparation.* 1. Iron-plate cut into strips is gently heated in a covered crucible with sulphur not in excess, and the resulting sulphide separated by bending the iron. Sulphide of iron thus obtained is free from excess of sulphur. If the heat applied is too strong, the sulphide fuses together with the remaining iron; if the sulphur is in excess, magnetic pyrites is formed. (Berzelius.)—2. By igniting iron-filings with two-thirds their weight of sulphur in a covered earthen or cast-iron crucible. The iron-filings are either disposed in a layer above the sulphur or the two are mixed (II, 221, *a* and *b*). In either case, the crucible is surrounded and covered with dead coals, and a few live coals laid upon the top; as soon as the whole is red-hot, the door of the furnace is closed. (Proust, *J. Phys.* 91, 271.)—3. Sulphur is held against a red-hot iron-bar, and the sulphide of iron, as it runs off, allowed to drop into water; or a bar of iron is repeatedly heated to whiteness and dipped into melted sulphur contained in a cast-iron crucible and frequently renewed. (Gahn.)—4. A finely divided mixture of scale-oxide of iron and sulphur is heated to redness.—5. Iron pyrites is heated to redness, either alone or with a small quantity of iron-filings. The methods 2, 3, 4, and 5 may likewise yield the following sulphur compound, corresponding to magnetic pyrites; but when sulphide of iron is heated till it fuses, the residue, according to Bredberg, always consists of protosulphide of iron.—6. By igniting anhydrous ferrous sulphate in a crucible lined with charcoal. The product contains, however, only 34 per cent. of sulphur, likewise more or less carbon. (Berthier, *Ann. Chim. Phys.* 22, 241.)—7. By igniting 1 part of iron-filings with 1 part of charcoal-powder and 4 parts of lead-sulphate, whereby metallic lead is obtained at the same time. (Fischer, *N. Tr.* 6, 1, 298.) — Yellow, with metallic lustre; yields a yellowish powder; it is attracted by the magnet. The protosulphide obtained by fusing iron pyrites is less hard than the bisulphide, and, on exposure to the air, crumbles to a bulky powder which emits a disagreeable odour when touched with wet hands.

Hydrated Protosulphide of Iron, or *Hydrosulphate of Ferrous Oxide.* 1. Alkaline hydrosulphates form with ferrous salts a black flocculent precipitate.—2. Twenty-seven parts of iron-filings and 16 parts of sulphur made into a paste with water, and kept out of contact of air, aggregate into a black mass, with strong evolution of heat; this effect takes place more quickly on the application of heat.—3. Iron-filings in contact with sulphuretted hydrogen water liberate hydrogen gas almost free from sulphur, and turn black; part of the resulting hydrosulphate of ferrous oxide dissolves in the water. (Vauquelin.)—The black compound oxidates quickly in the air, forming water, ferric oxide, and sulphur or sulphuric acid; and, even if it be kept for several weeks before being exposed to the air, the action is attended with an evolution of heat, which, if the mass is considerable, may even produce inflammation. The *Artificial Volcanos of Lemery* are formed by mixing several pounds of iron-filings with $\frac{1}{4}$ to $\frac{2}{3}$ of its weight of sulphur, making the mixture into a paste with water, and burying it in the ground.—Hydrated protosulphide of iron decomposes the salts of cadmium, lead, copper and silver, precipitating the metals as sulphides. (Anthon.)—It dissolves in dilute acids much more quickly than the anhydrous sulphide, and with violent evolution of sulphuretted hydrogen.—It dissolves in small quantity in water (especially in hot water: *Berzelius*), forming a solution which has a dark green colour and inky taste. (Vauquelin, *Scher. J.* 6, 63; also *Gilb.* 9, 42.) The presence of hydrosulphuric acid or hydrosulphate of ammonia in the water prevents the solution; and any sulphide of iron previously dissolved in pure water is precipitated on the addition of hydrosulphate of ammonia and the application of heat. (Berzelius.) According to later investigations of Vauquelin (*J. Pharm.* 13, 266), iron-filings and sulphuretted hydrogen water, placed together in a close vessel for four-and-twenty hours, yield, after filtration, a colourless solution which blackens quickly on exposure to the air. According to O. Henry (*J. Pharm.* 24, 118), when a solution of green vitriol is precipitated with excess of aqueous sulphide of calcium, a small quantity of iron still remains dissolved.

The black mud at the bottom of drains contains hydrated sulphide of iron, probably formed by the putrefaction of organic substances in contact with the ferric oxide of earthy matters, and to this it owes its black colour and peculiar smell. Hence, when exposed to the air, it loses its odour and colour, and afterwards resembles ordinary vegetable mould. With hydrochloric acid it evolves abundance of sulphuretted hydrogen; to boiling potash it gives up sulphuretted hydrogen together with organic matter. The black colour of the soil in privies, pits, ponds and morasses, and of the sand between the pavement of streets [also of fæces after the administration of medicines containing iron] is likewise due to hydrated sulphide of iron. (Braconnot, *Ann. Chim. Phys.* 50, 213.)

D. Eight-sevenths Sulphide of Iron.—Found native in the form of *Magnetic Pyrites.* This mineral crystallizes in forms belonging to the hexagonal system. *Figs.* 132, 135, 136, 137, 138 and others. $p:r$ (*Fig.* 132)$=102°\ 13'$; $p:r$ (*Fig.* 136)$=105°$. Cleavage parallel to p. Harder than calcspar; sp. gr. 4·5 to 4·7; brittle; with conchoidal fracture. Colour varying from bronze-yellow to brown; powder greyish-black. Acted on by the magnet, and often itself magnetic. According to Berzelius, it does not give off sulphur when ignited out of contact of air. Fuses on charcoal before the blowpipe, forming a greyish-black, *strongly magnetic* globule. When roasted in the state of fine powder, it

is converted into pure ferric oxide. When ignited in a current of hydrogen gas, it loses so much sulphur that it is converted into the protosulphide. (The same result was obtained by Plattner, *Pogg.* 47, 369.) It likewise gives up its excess of sulphur to boiling caustic potash, while a mass resembling the hydrated protosulphide remains behind. (Count Schaffgotsch, *Pogg.* 50, 533.) When heated to whiteness in a charcoal crucible, it diminishes in weight but slowly. It exhibits the same decompositions as the protosulphide, excepting that, when it is dissolved in dilute hydrochloric or sulphuric acid, not only is hydrosulphuric acid gas evolved, but sulphur is likewise precipitated in the form of powder. (Stromeyer.) The separated sulphur is dark grey, because it contains undecomposed sulphide of iron. (Schaffgotsch.)

According to Berzelius, the same compound, and not the protosulphide, is formed by igniting iron or the scale-oxide with excess of sulphur, by heating iron pyrites to redness, and by igniting the one-eighth sulphide or the disulphide of iron in hydrosulphuric acid gas.—The artificial compound is brownish bronze-yellow and susceptible of magnetic action, and, according to Hatchett (*Gilb.* 25, 58), may likewise be rendered permanently magnetic.

					Schaffgotsch.		H. Rose.		Stromeyer.
	Magnetic Pyrites.				Bodenmais.				Preseburg.
7Fe	189	....	59·62	....	60·59	....	60·95	....	59·85
8S	128	....	40·38	....	39·41	....	39·05	....	40·15
$6FeS,FeS^2$	317	....	100·00	....	100·00	....	100·00	....	100·00

			Plattner.		Stromeyer.
	Fahlun.		Brazil.		Barèges.
Fe	59·72	....	59·64	....	53·37
S	40·22	....	40·43	....	43·63
	99·94	....	100·07	....	100·00

For analyses of magnetic pyrites, in which a small part of the iron is replaced by nickel, *vid.* Th. Scheerer (*Pogg.* 58, 318), and Berzelius (*Jahresber.* 21. 2, 184).

E. Sesquisulphide of Iron, or Ferric Sulphide.—1. Formed by heating protosulphide of iron mixed with sulphur to very low redness, till the excess of sulphur is expelled. (Proust, *Scher. J.* 10, 54; also *Gilb.* 25, 54. Bucholz & Gehlen, *N. Gehl.* 9, 291.)—2. By passing hydrosulphuric acid gas over ferric oxide heated not above 100°, as long as water continues to be formed. The transformation goes on without any alteration of form; the artificial hydrated sesquioxide is decomposed, even at ordinary temperatures, with slight evolution of heat, only requiring the heat of a water-bath towards the end of the operation; the moisture is afterwards driven off in vacuo. (Berzelius.)—Greenish-yellow (Proust); yellowish-grey (Bucholz & Gehlen, Berzelius); acquires a higher polish under the burnishing steel, and when gently heated in vacuo, becomes yellower and more lustrous (Berzelius). Magnetic, according to Proust; non-magnetic, according to Berzelius.

					Proust.		Bucholz & Gehlen.
2Fe	54	....	52·94	....	52·64	....	52·64 to 52·07
3S	48	....	47·06	....	47·36	....	47·36 „ 47·93
Fe^2S^3	102	....	100·00	....	100·00	....	100·00 „ 100·00

By stronger ignition it gives off sulphur, and is reduced to the eight-sevenths sulphide. In the dry state it remains unaltered in the air, but

if exposed while yet moist—as in the state in which it is obtained by the action of surphuretted hydrogen on ferric oxide at ordinary temperatures—it is completely converted, in the course of a few hours, into a mixture of ferric oxide and sulphur. By dilute hydrochloric or sulphuric acid, it is converted into sulphuretted hydrogen, a ferrous salt, and bisulphide of iron, which latter still retains the form of the sesquisulphide; but, so long as it remains moist, may be reduced by pressure to the finest powder. (Berzelius.)

Hydrated Sesquisulphide of Iron, or *Hydrosulphate of Ferric Oxide.*—Formed by dropping an aqueous solution of a ferric salt into an excess of alkaline hydrosulphate. If, on the contrary, the alkaline hydrosulphate be dropped into an excess of the ferric salt, sulphur is first precipitated and a ferrous salt produced, from which an additional quantity of alkaline hydrosulphate throws down hydrosulphate of ferrous oxide.—Black precipitate, which oxidizes quickly in the air. (Berzelius.)

F. Bisulphide of Iron.—Found in nature as *Iron Pyrites* (*Schwefelkies* or *Eisenkies*), and as *White Iron Pyrites, Radiated Iron Pyrites*, or *Cockscomb Pyrites* (*Strahlkies, Wasserkies*, or *Speerkies*). Each of these varieties of iron pyrites is often produced by the action of organic substances on water containing iron, together with salts of sulphuric acid. On a sand-heath overgrown with *Erica*—the root-stratum of which smelt strongly of hydrosulphuric acid—portions of the *Arundo Phragmites* were found to be partially covered with steel-grey laminæ and crusts of a sulphide of iron not soluble in dilute hydrochloric acid. (Meinecke, *Schw.* 28, 56.)—Link found iron pyrites in the mud of ponds.—Bakewell found the remains of mice preserved in a bottle filled with solution of green vitriol, covered with small crystals of iron pyrites.—The hot spring of Chaudesaigues, which contains sulphate of soda and other salts and a mere trace of iron, deposits iron pyrites in the [wooden?] channel by which the water is discharged. (Longchamp, *Ann. Chim. Phys.* 32, 294.) On digging in the neighbourhood of the chalybeate spring at Röndorfer, which contains acid carbonate of ferrous oxide and sulphate of soda, the boggy ground and the fragments of quartz scattered about, were found to be covered with iron pyrites. (Nöggerath & Bischof, *Pogg.* 38, 407.)—A similar case is described by Gilbert. (*Gilb.* 74, 206.)—A ferruginous water which ran from a basin formed out of the hollow trunk of a tree, yielded, when recently drawn, a large quantity of blackish-yellow iron pyrites, containing a portion of vegetable matter enclosed within it, and, moreover, 44·78 iron to 55·22 sulphur.—A quantity of the Brohl mineral water, which contains very small quantities of iron and sulphate of soda, having been mixed with a little sugar and kept for three years in closed vessels, was found to smell of sulphuretted hydrogen, and had deposited a black powder which appeared to contain sesquisulphide of iron together with free sulphur. In a similar manner, white iron pyrites appears to be formed in black and in brown coal. (Bischof, *Schw.* 64, 377.)

Preparation. 1. Ferric oxide, ferroso-ferric oxide, hydrated ferric oxide or carbonate of ferrous oxide, natural or artificial, in powder or in crystals, is exposed, at a heat exceeding 100° but not amounting to redness, to a current of sulphuretted hydrogen, as long as the mass continues to increase in weight. At first the action is so strong, that aqueous vapour, sulphurous acid, and hydrogen gas are evolved, and lower sulphides of iron are formed, which afterwards take up more sulphur and liberate pure

hydrogen gas. The sulphide of iron thus produced retains the crystalline form of the oxide used in its preparation, with the same lustre on the faces, and the same directions of cleavage. (Berzelius.)—2. The lower sulphides of iron may be brought to this, the highest degree of sulphuration, by heating them in like manner in hydrosulphuric acid gas. (Berzelius.)—3. An intimate mixture of 2 pts. protosulphide of iron and 1 pt. sulphur, heated in a retort to a temperature short of redness, leaves bisulphide of iron in the form of a bulky, dark yellow, non-magnetic, metallic powder, not attacked by hydrochloric acid. (Berzelius.)—4. When an intimate mixture of ferric oxide, sulphur, and sal-ammoniac is heated to a temperature a little above that at which the sal-ammoniac sublimes, the residue is found to contain small, brass-yellow octohedrons and cubes, which may be separated from the rest of the powder by levigation. (Wöhler, *Pogg.* 37, 238.)—5. When sal-ammoniac containing sulphate of ammonia is sublimed at a dull red heat in iron vessels coated with clay, the clay covering becomes impregnated with chloride of iron, and cubes and octohedrons of iron pyrites form upon its surface. (Löwe, *J. pr. Chem.* 6, 98.)

Iron pyrites crystallizes in forms belonging to the regular system: *Figs.* 1, 2, 4, 6, 11, 18, 19, 20, and many others. It gives sparks with steel. Sp. gr. 4·9 to 5·1. Fracture, conchoidal. Colour, bronze-yellow. The crystals of white iron pyrites belong to the right prismatic system: *Fig.* 54, 61, and other forms, $u : u'$ (*Fig.* 54)$=73° 24'$; $u' : u$ (*Fig.* 61) $=106° 36'$, $i : i'=32° 12'$. Cleavage parallel to u and u', less distinct parallel to p. (Hauy.) Sp. gr. 4·6 to 4·8. Harder than felspar. Greenish-yellow-grey inclining to steel-grey; powder greenish-grey.—Iron pyrites is non-magnetic in all its forms.

Ordinary Iron Pyrites.

			Berzelius.	Hatchett.	Gueniveau.
Fe	27	45·77	46·08	45·7 to 47·8	46·6 to 47·24
2S	32	54·23	53·92	54·3 „ 52·2	53·4 „ 52·76
FeS^2	59	100·00	100·00	100·0 100·0	100·0 100·00

White Iron Pyrites.

	Bucholz.		Berzelius.
Fe	49	.....	45·07
S	51	.....	53·35
		Mn	0·70
		SiO^2	0·80
FeS^2	100	.....	99·92

Bisulphide of iron ignited not very strongly in a close vessel, gives off sulphur, and is converted into the eight-sevenths sulphide; at a strong red heat it is reduced to the protosulphide. A lower temperature will suffice if hydrogen gas be passed over the substance, although the hydrogen does not form hydrosulphuric acid, but appears to act like any other gas [by adhesion]. (H. Rose, *Pogg.* 5. 533.)—The residue has the form and colour of the original iron pyrites, but its bulk is increased; it is dull, exhibits all over its surface cavities formed by fusion, and may be crumbled to pieces by pressure with the finger. (Proust, *Scher. J.* 9, 378.)—When ignited with charcoal it yields bisulphide of carbon.—When heated in a current of phosphuretted hydrogen gas to a temperature short of that at which it evolves sulphur, it yields phosphide of iron and hydrosulphuric acid. (p. 233.)—When heated in the air, it yields sulphurous acid

and sulphate of ferrous oxide, or, at a higher temperature, sulphurous acid and basic sulphate of ferric oxide.

With nitric or nitro-hydrochloric acid, it yields ferric oxide, sulphuric acid, and sulphur. It resists the action of hydrochloric and of dilute sulphuric acid.—Iron pyrites heated with lead-oxide, fuses readily and gives off sulphur in the form of sulphurous acid; for the complete expulsion of the sulphur, 50 parts of lead-oxide are required to 1 part of pyrites. With 6 parts of litharge to 1 iron pyrites, 2 layers are obtained; the lower, which contains the larger quantity of matter, is a sulphide of lead containing excess of lead; the upper layer is a lead-grey, magnetic mixture of sulphide of lead, sulphide of iron, and metallic oxides.—With 12·5 pts. litharge, the mixture yields 3·5 pts. of lead, rendered somewhat brittle by the presence of 1 per cent. of sulphur and a small quantity of iron, together with a black, opaque, vitreous slag.—With 20 parts of litharge, the same products are formed, the lead, which in this case also is somewhat brittle, amounting to 4 parts. With 30 parts of litharge, 4·55 parts of lead are obtained; with 40 pts. litharge, 5·48 lead; and with 50 litharge, 8·6 lead, together with a transparent red glass. The quantity of lead does not exceed 8·6 parts, even if more than 50 parts of litharge are used. (Berthier, *Ann. Chim. Phys.* 39, 253.)

Most yellow iron pyrites, and likewise the white variety when well crystallized, remain unaltered in moist air. But many crystals of auriferous iron pyrites exhibit marks of conversion into hydrated ferric oxide, and white iron pyrites often becomes quickly covered with effloresced ferrous sulphate.—The efflorescence shows itself only on irregularly crystallized masses of the white pyrites, such masses containing protosulphide of iron mixed with the bisulphide. The latter only is made to effloresce by being formed into a galvanic circuit with the more negative bisulphide. Hence the ferrous sulphate which effloresces out contains but 1 atom of sulphuric acid, and when dissolved in water deposits ochre on exposure to the air, whereas if formed from the bisulphide, it would have contained 2 atoms of acid. The bisulphide remains quite unaltered; is split up by the crystals of ferrous sulphate; and after being washed with water shows no traces of free sulphur. A mass which will effloresce in 12 hours and expand to a tenfold bulk in 4 days by formation of green-vitriol crystals, may be artificially produced by exposing ferric oxide to the action of hydrosulphuric acid, and stopping the process before the conversion into bisulphide is complete, so that some of the lower sulphides of iron may remain mixed with it. The same considerations serve to explain why iron pyrites exposed to imperfect ignition, whereby a part only of the bisulphide of iron is converted into protosulphide, acquires a tendency to effloresce. (Berzelius.)—Fournet (*Ann. Chim. Phys.* 55, 256) attributes the efflorescing property of white iron pyrites to a forced state of aggregation of the particles.—The ferrous sulphate effloresced out of the white iron pyrites of Schriesheim, when extracted by water, was found by the author to yield a solution which did not become at all turbid by the addition of a small quantity of potash or by prolonged exposure to the air; and the washed residue contained free sulphur which showed itself in yellow specks and could be extracted by caustic potash (compare also H. Rose, p. 245).—Since the efflorescence of sulphide of iron is attended with evolution of heat, we may hence account for the inflammation of coals containing that mineral, when they are heaped up in considerable masses (either within or without the mine) and exposed to air and moisture. (Berzelius.)

G. *Sulphide of Ferrous Oxide?*—Formed by heating ferric oxide with powdered sulphur to a temperature short of redness, till sulphurous acid gas is no longer evolved.—Chesnut-brown powder, attracted by the magnet.—Dissolves with difficulty in hydrochloric acid, sulphur being precipitated but no sulphuretted hydrogen evolved. Takes fire in the air below a red-heat, burning like tinder, and being thereby completely converted into ferric oxide. (Berzelius.)

H. Hyposulphite of Ferrous Oxide, or Ferrous Hyposulphite. —Iron immersed in aqueous sulphurous acid and kept from contact of air dissolves without evolution of gas, and forms sulphite and hyposulphite of ferrous oxide:

$$2Fe + 3SO^2 = FeO, SO^2 + FeO, S^2O^2.$$

The iron immediately becomes black and brittle by taking up sulphur. (Berthollet, *Ann. Chim.* 2, 58.) The iron dissolves completely with the exception of a few black flakes arising from impurities in the metal. (Fordos & Gélis, *N. J. Pharm.* 4, 333.) The sulphurous acid, in acting upon the iron, becomes first brown, then yellow, and afterwards transparent and colourless, the last change being attended with precipitation of sulphur; no hydrosulphuric acid is evolved, although the liquid contains a small quantity of that gas while it is in the yellow state, and therefore blackens paper moistened with acetate of lead. The resulting solution turns brown when heated, and yields a reddish precipitate; on the addition of hydrochloric acid, sulphurous acid is evolved and sulphur precipitated. The solution gives with alkalis and with ferrocyanide of potassium a white precipitate; with mercurous and mercuric salts, a black precipitate containing globules of mercury; and with nitrate of silver, a white precipitate which afterwards blackens. (A. Vogel, *J. pr. Chem.* 8, 102; *vid.* also Köne, *Pogg.* 63, 145.)—If very strong sulphurous acid is used, part of the ferrous sulphite crystallizes out spontaneously in the course of a few days, in white or greenish-white crystals. (Berthollet, A. Vogel.) By evaporating and cooling the solution out of contact of air, the greater part of the ferrous sulphite is separated out in the crystalline form, and the mother-liquid when evaporated in vacuo (great care being taken to prevent ingress of air) yields crystals of the hyposulphite, which, however, are frequently contaminated with sulphur and green vitriol. For, in proportion as the air acts upon the colourless mother-liquid containing the ferrous hyposulphite, that liquid acquires a yellow colour from formation of ferric hyposulphite. During the subsequent evaporation, even in vacuo at ordinary temperatures, the ferric oxide converts the hyposulphurous acid into tetrathionic acid:

$$Fe^2O^3 + 2S^2O^2 = 2FeO + S^4O^5;$$

and the tetrathionate of ferrous oxide thus produced is resolved by further evaporation into sulphur, sulphurous acid, and green vitriol:

$$FeO, S^4O^5 = FeO, SO^3 + SO^2 + 2S.$$

(Fordos & Gélis.) ¶ Köne separates the sulphite and hyposulphite of ferrous oxide obtained as above, by means of alcohol, in which the hyposulphite is easily soluble, while the sulphite is insoluble ¶. By precipitating green vitriol with hyposulphite of baryta, and evaporating the filtrate, green crystals are obtained, mixed with a basic salt of ferric oxide. (Rammelsberg, *Pogg.* 56, 306.)

Besides the soluble salt just described, there likewise exists an insoluble hyposulphite of ferric oxide. When steel turnings (iron would probably act in the same way) are immersed for 14 days in a saturated aqueous solution of sulphurous acid contained in a closed vessel, the transparent and colourless liquid poured off, and the black steel turnings washed with water,—small, translucent, greenish-white octohedrons are found adhering to their surfaces. These crystals do not fuse when heated, but evolve sulphurous acid together with a small quantity of sulphur: by exposure to the air, they become opaque and afterwards of a rust colour. With strong hydrochloric acid they effervesce violently, give off sulphurous acid gas, and form a yellow solution from which sulphur is deposited; their powder turns black when moistened with solution of silver; they are insoluble in water, not even boiling water taking up a trace of iron; aqueous sulphurous acid dissolves them slowly. (A. Vogel.)

I. Sulphite of Ferrous Oxide, or Ferrous Sulphite.—The solution of iron in aqueous sulphurous acid formed out of contact of air (which likewise contains ferrous hyposulphite: *vid. sup.*) deposits, either immediately or when evaporated out of contact of air, crystals of ferrous sulphite, that salt separating out before the hyposulphite. (Berthollet.) The solution should be evaporated in vacuo, the crystals pressed between bibulous paper and then dried in vacuo. (Fordos & Gélis.)—When heated in a glass tube, they evolve sulphurous acid and water and leave a black residue. While yet moist, they oxidate in the air. They dissolve very sparingly in pure water, easily in aqueous sulphurous acid. This solution soon acquires a deep red colour by exposure to the air. (Fordos & Gélis.)

Crystallized.	Calculation, according to Fordos & Gélis.		
FeO	35		37·23
SO^2	32		34·04
3HO	27		28·73
$FeO,SO^2+3Aq.$	94		100·00

K. Sulphite of Ferric Oxide, or Ferric Sulphite.—Freshly precipitated hydrate of ferric oxide dissolves readily in aqueous sulphurous acid, but the solution which is red at first, quickly becomes decolorized by formation of ferrous sulphate. The dry hydrate dissolves but very sparingly in cold sulphurous acid; the hot acid dissolves it quickly, but the solution consists of ferrous sulphate.—¶ According to Köne, if the excess of sulphurous acid be expelled by heat and the solution then left exposed to the air for several days, a red-brown precipitate is obtained, composed of $Fe^2O^3,SO^3+7Aq.$ (*Ann. Pharm.* 64, 241) ¶.—2. Alkaline sulphites impart a deep red colour to ferric salts, even when largely diluted; but the mixture soon loses its colour even at ordinary temperatures, and immediately on the application of heat. (Berthier, *Ann. Chim. Phys.* 50, 370; *N. Ann. Chim. Phys.* 7, 78.)

L. Hyposulphate of Ferrous Oxide, or Ferrous Hyposulphate—Formed by precipitating a solution of green vitriol by an exactly equivalent quantity of hyposulphate of baryta, and leaving the filtrate first to evaporate at a gentle heat and then to crystallize by spontaneous evaporation.—Oblique rhombic prisms, having the colour and taste of green vitriol. They become somewhat brown in the air by oxidation, but *without* further change. When carefully heated, they leave 49·05 per

cent. of dry ferrous sulphate. Very easily soluble in water, but not in alcohol; when the aqueous solution is boiled, the salt is converted into green vitriol. (Heeren.)

	Crystallized.				Heeren.
FeO	35	....	23·03	.....	22·91
S^2O^5	72	....	47·37	.....	47·05
5HO	45	....	29·60	.....	30·04
$FeO, S^2O^5 + 5Aq$	152	....	100·00	.....	100·00

M. Hyposulphate of Ferric Oxide, or Ferric Hyposulphate.—*Octobasic.*—Aqueous hyposulphuric acid dissolves but a very small quantity of hydrated ferric oxide, even when freshly precipitated; it however combines with the oxide and forms a brown-red, very soft, easily suspended powder, which dries up to a brown, brittle mass having a conchoidal fracture and easily soluble in hydrochloric acid. (Heeren.)

					Heeren.
$8Fe^2O^3$	624	....	71·23	....	69·99
S^2O^5	72	....	8·22	....	8·25
20HO	180	....	20·55	....	21·76
$8Fe^2O^3, S^2O^5 + 20Aq.$	876	....	100·00	....	100·00

N. Sulphate of Ferrous Oxide, or Ferrous Sulphate.—*Protosulphate of Iron, Green Vitriol, Copperas.*—This salt is formed in mines containing sulphide of iron, and dissolves in the water of the mine.—Dilute sulphuric acid dissolves iron with evolution of hydrogen gas. Strong oil of vitriol dissolves it slowly at ordinary temperatures with evolution of hydrogen gas—more quickly when heated, and with evolution of sulphurous acid gas. Moist or heated sulphide of iron is converted by exposure to the air into green vitriol (pp. 229 and 234).—The crystallized salt is prepared on the small scale by dissolving iron in dilute sulphuric acid, filtering, evaporating, and crystallizing. On the large scale, it is prepared in an impure state, by exposing native sulphide of iron to the action of the air—or first roasting and then exposing it to the air,—and afterwards exhausting with water, evaporating, clarifying, and cooling.—When iron is immersed in mine-water containing sulphate of copper, the copper is precipitated, and a dilute solution of green vitriol is obtained, which may be brought to the crystallizing point, first by *graduation*, and afterwards by evaporation. The commercial green-vitriol from Fahlun and Dylta, and that also which is prepared in England, is crystallized from an acid solution, contains but little ferric sulphate, is of a greenish-blue colour, and often covered with a white or yellow powder. The German green-vitriol, which is crystallized from a more neutral solution, and contains but a small quantity of ferric salt, is of a dirty green colour and dry. That from Moscow is crystallized from a solution containing a considerable quantity of ferric salt, and is therefore mixed with that salt; it has a grass-green colour and unctuous aspect, because it remains moist; it also reddens litmus strongly. (Bonsdorff.)—Besides ferric sulphate, commercial green vitriol may also contain protoxide of copper, oxide of zinc, binoxide of tin, protoxide of manganese, alumina, magnesia, and lime in the state of sulphates, and likewise arsenious acid.—The cupric and ferric oxides may be separated by mixing the aqueous solution with a small quantity of sulphuric acid and digesting it with metallic iron out of contact of air; and the arsenic, copper, and tin, by saturating the solution with sulphuretted hydrogen, setting it aside for two days, and then warming and filtering.

In consequence of the great facility with which ferrous sulphate absorbs oxygen from the air, the crystals are very apt to become contaminated with ferric sulphate. Green vitriol free from ferric oxide may be obtained by the following processes: 1. By saturating dilute sulphuric acid with iron, boiling the liquid with iron-filings in a narrow-necked flask, till the crystallizing point is attained, and straining it through a filter moistened with water, into a vessel rinsed out with a little dilute sulphuric acid. The sulphuric acid prevents the filtrate from becoming turbid. The funnel must have a very long neck reaching to the bottom of the vessel. The crystals, as they form, are left to drain upon a funnel, then rolled backwards and forwards between bibulous paper, till they no longer wet it, and dried upon paper at a temperature not exceeding 30°. When well dried, they remain permanent for a long time in dry air, and for a tolerably long time in damp air. (*v.* Bonsdorff, *Pogg.* 31, 81.)—2. By dissolving 200 parts of iron-filings in 2,400 of water, to which 300 of oil of vitriol is gradually added, evaporating the liquid to the crystallizing point in a cast-iron vessel; mixing it with 15 parts of oil of vitriol; filtering hot; cooling; pressing the crystals to powder as soon as they are formed; washing with alcohol, and quickly drying the bluish-white powder between bibulous paper. (Gieseler, *N. Br. Arch.* 27, 193.)—3. By leaving good green vitriol to crystallize from water acidulated with sulphuric acid; boiling 500 parts of the resulting crystals, for a while, with 550 parts of water and 8 parts of iron-turnings, and filtering the solution at a boiling heat into a vessel containing a mixture of 375 pts. alcohol of 36° B., and 8 parts of oil of vitriol, the mixture being stirred all the while. After cooling, the mother-liquid is strained off from the small crystals which form, the crystals drained upon linen, and then dried between bibulous paper frequently renewed. The alcohol retains in solution the whole of the ferric salt, the solubility of that salt being increased by the free sulphuric acid. The crystals contain their full amount of water. (Berthemot, *J. Pharm.* 25, 206.)

By heating the crystals out of contact of air, the anhydrous salt is obtained in the form of a white, harsh powder.—This when heated in a retort, gives off sulphurous acid gas, and is converted into a compound of 1 At. ferric oxide and 1 At. sulphuric acid:

$$2(FeO,SO^3) = Fe^2O^3,SO^3 + SO^2.$$

At a still higher temperature, the rest of the sulphuric acid is given off, and red ferric oxide left behind. Part of the acid distils over undecomposed, and may be condensed in the form of anhydrous acid in a receiver kept at a very low temperature; the rest passes over as a mixture of 1 vol. oxygen, and 2 vol. sulphurous acid gas. (Bassy.)—When moderately heated in an open vessel and stirred, it is converted—the ferrous oxide taking up oxygen from the air—into yellowish-brown *burnt* or *calcined green vitriol*, containing 1 At. ferric oxide and 2 At. sulphuric acid. Complete conversion into ferric salt is unattainable; as soon as all the protoxide is converted into sesquioxide, sulphuric acid is given off, and colcothar remains behind. (Waltl, *Repert.* 41, 428.) Dry ferrous sulphate gently ignited with charcoal in a retort, gives off about 78 volumes of sulphurous acid gas to 22 vol. carbonic acid, and leaves ferric oxide free from sulphide of iron. (Gay-Lussac, *Ann. Chim. Phys.* 63, 433; also *J. pr. Chem.* 11, 67.)

				Berzelius.	Wenzel.
FeO	35	46·66	47·07	42·17
SO^3	40	53·33	52·93	57·83
FeO,SO^3	75	100·00	100·00	100·00

Combinations with Water.—The dehydrated salt recovers its 7 atoms of water by exposure to moist air. (Brandes, *Schw.* 51, 438.)—*α. Mono-hydrated.*—Remains when the hepta-hydrated salt is heated to 140° in vacuo; contains 1 atom of water in a state of intimate combination, but gives it up at a temperature above 280° (between 200° and 300°, Mitscherlich, *Pogg.* 18, 152), and by careful heating may be freed from it without loss of acid. (Graham, *Phil. Mag. J.* 3, 421.)

β. Bihydrated.—When oil of vitriol is slowly added to a saturated solution of ferrous sulphate—so as not to produce any considerable rise of temperature—till the mixture attains a specific gravity of 1·33, and the liquid then left to evaporate over oil of vitriol in a receiver not exhausted of air, the hepta-hydrated salt separates out first; then, when $\frac{2}{3}$ of the liquid are evaporated, a salt containing 4 atoms of water; then sesqui-sulphate of ferrous oxide (p. 242); and lastly, the bihydrated salt in the form of a dark green, crystallo-granular mass. (v. Bonsdorff, *Ber. über d. Versamml. d. deutschen Naturf. in Prag.* 124.)

γ. Ter-hydrated.—The solution of green vitriol in hot hydrochloric acid, yields on cooling, partly crystals of the hepta-hydrated, and partly of the ter-hydrated salt. The latter are translucent, of a much paler green colour, and harder than the former; when dissolved in water, they again yield ordinary green vitriol. (Kane, *Ann. Pharm.* 19, 7.)—On evaporating a solution of green vitriol mixed with a large quantity of sulphuric acid, the ter-hydrated salt is obtained in the form of a white solid crust. (Kühn, *Schw.* 61, 235.)

			Kane.	Kühn.
FeO	35	34·31	33·4	34·3
SO^3	40	39·22	37·4	39·0
3HO	27	26·47	29·2	26·7
$FeO,SO^3+3Aq.$	102	100·00	100·0	100·0

δ. Tetra-hydrated.—1. By the process described under β, this salt is obtained in crystals having the green colour of *Chrysoprase.* (Bonsdorff.) —2. It crystallizes on evaporating a solution of green vitriol at 80°, and corresponds to the tetra-hydrated sulphate of manganous oxide. (IV., 222.) Regnault. (*N. Ann. Chim. Phys.* 1,201.)

ε. Hepta-hydrated.—This is the common green vitriol.—Pale greenish-blue, translucent crystals, belonging to the oblique prismatic system. *Fig.* 111 and other forms; $i:u$ or $u'=99°\ 2'$; $u:u'=82°\ 20'$; $i:\alpha=153°$; $i:\beta=123°\ 55'$; $i:c=159°$; $i:d=136°\ 10'$; $i:f=119°\ 15'$. (Wollaston, *Schw.* 24, 102; Brooke, *Ann. Phil.* 22, 120; G. Rose, *Pogg.* 7, 239.) Yields a white powder; scarcely reddens litmus, and only when the air has access to it, the effect being then due to the formation of a ferric salt. (Bonsdorff.)

			Berzelius.	Bergman.	Kirwan.	Thomson.	Mitscherlich.
FeO	35	25·36	25·7	23	28	28·3	56·08
SO^3	40	28·98	28·9	39	26	26·7	
7HO	63	45·66	45·4	38	46	45·0	43·92
$FeO,SO^3+7Aq.$	138	100·00	100·0	100	100	100·0	100·00

The crystals fuse in their water of crystallization when heated; and if the air be excluded, leave the white anhydrous salt. When exposed to the air between 40° and 50°, they effloresce through and through to a white mass (Bonsdorff); oil of vitriol and alcohol likewise withdraw their water and cause them to turn white. At ordinary temperatures, they oxidize and turn brown, in proportion as they have been less completely dried, as the air is moister, and as the solution from which they have been formed is more neutral. Crystals obtained from an acid solution are permanent in air which is not very damp; but if they are kept under a bell-jar containing air, and closed with water at the bottom, their surface turns yellowish-brown in the course of a few months, a portion of the salt being at the same time dissolved by the water which is deposited. Crystals deposited from a perfectly neutral solution, assume a dingy green colour when exposed to the air even for a few days, the colour continually becoming darker; under a bell-jar standing in water, they deliquesce more rapidly and soon turn brown. The powder of crystals obtained from an acid solution turns yellowish-green after a few weeks' exposure to the air.

1 part of the crystals dissolves in 1·6 parts of cold, and in 0·3 of boiling water. At 10° in 1·64 parts; at 15° in 1·43; at 24° in 0·87; at 33° in 0·66; at 46° in 0·44; at 60° in 0·38; at 84° in 0·37; at 90° in 0·27; and at 100° in 0·3 parts of water. (Brandes & Firnhaber. *Br. Arch.* 7, 83.)—The solution has a pale greenish-blue colour. Alcohol and oil of vitriol precipitate from it the white, partly dehydrated salt. Glacial acetic acid likewise precipitates the salt undecomposed from the solution, so that not a trace of iron is left in the liquid. (Persoz, *Chim. molecul.* 346.) The solution becomes turbid when exposed to the air, yellowish-brown disulphate of ferric oxide being precipitated, and tersulphate being dissolved and forming a brown solution;

$$10(FeO,SO^3)+5O = 2Fe^2O^3,SO^3+3(Fe^2O^3,3SO^3).$$

On the addition of sal-ammoniac, a solution is formed, consisting of sulphate and hydrochlorate of ferrous oxide and ammonia. (A. Vogel, *J. pr. Chem.* 2, 192.)

A solution of green vitriol absorbs nitric oxide gas, forming a dark greenish-brown liquid, which contains 1 at. nitric oxide to 4 at. oil of vitriol. The solution of 300 pts. (1 at.) of dry ferrous sulphate, absorbs 28·5 pts. (therefore not quite 1 at., which would weigh 30) of nitric oxide. If the sulphuric acid is in excess, the same quantity of nitric oxide gas is absorbed, and produces the same colour. (Peligot.)—The liquid contains ferrous sulphate and nitric oxide in the unaltered state; the latter may be driven off in vacuo, or by the application of heat; but in the latter case, a small portion of the nitric oxide gives up oxygen to the ferrous oxide, so that the evolution of nitric oxide is accompanied by the conversion of a small portion of ferrous salt into ferric salt. If the liquid be placed, together with chloride of calcium, under a bell-jar filled with nitric oxide gas, ferric salt is formed and nitric oxide decomposed, as soon as the solution becomes somewhat concentrated.—An alkali added to the liquid produces a greyish-white precipitate, probably a compound of hydrated ferrous oxide with nitric oxide, which, however, soon gives off gas, turns bluish-green, and afterwards yellow. No salt of nitric or of nitrous acid is formed in this action.—Phosphate of soda forms a reddish-brown precipitate, which contains nitric oxide in a state of combination, and, when exposed to the

air, turns white and yields phosphate of ferric oxide. In a similar manner, ferrocyanide of potassium forms red-brown flakes, which contain nitric oxide and immediately turn blue in the air. (Peligot, *Ann. Chim. Phys.* 54, 17; also *J. Pharm.* 19, 644; also *Schw.* 69, 341; also *Ann. Pharm.* 9, 259.)—According to Sir H. Davy, 100 parts of green vitriol solution, of sp. gr. 1·4, absorb 0·63 nitric oxide, three-fourths of which remains unaltered, but the remaining fourth decomposes a portion of the water, and forms ammonia, nitric acid [?], and ferric oxide; a small quantity of nitrogen is likewise absorbed together with the nitric oxide, and is also converted into ammonia. The remaining three-fourths of undecomposed nitric oxide may be expelled from the liquid by heat. (Humboldt & Vauquelin, *Scher. J.* 3, 81.)

The compound of green vitriol with nitric oxide imparts a purple-red colour to large quantities of oil of vitriol, provided no rise of temperature takes place. Oil of vitriol, to which a small quantity of ferrous sulphate has been added, acquires a rose-red colour by absorbing small quantities of nitric oxide, and a deep purple-red if it absorbs a larger quantity. The same red mixture is obtained when oil of vitriol containing nitric oxide, nitrous or nitric acid, or a nitrate, is mixed with powdered green vitriol or its aqueous solution, slowly enough to prevent rise of temperature. Upon this character is founded the detection of those oxides of nitrogen in oil of vitriol (II. 181), and that of traces of nitrites and nitrates. (II. 401; Desbassins de Richemont, *J. Chim. méd.* 11, 504.)—Bussy & Lecanu (*J. Pharm.* 11, 341; also *Schw.* 46, 368), by dissolving ferrous sulphate in oil of vitriol, obtained a red liquid which they regarded as an acid sulphate of ferrous oxide. Their sulphuric acid evidently contained nitric oxide. When an aqueous solution of ferrous sulphate saturated with nitric oxide, is slowly mixed with oil of vitriol, the greenish-brown colour likewise changes to red. (Jacquelin, *N. Ann. Chim. Phys.* 7, 196.)

The red liquid loses its colour when heated, giving off sulphurous acid, and precipitating white tersulphate of ferric oxide. Water carefully added, so as not to occasion rise of temperature, gradually dilutes the colour, till it finally becomes imperceptible. (Bussy & Lecanu.) Water decolorizes the solution, after first turning it brown and yellow. (Desbassins.) Compounds which convert the ferrous oxide into ferric oxide, destroy the colour, and produce a white cloud, proceeding from tersulphate of ferric oxide. Such is the action produced by nitric and its salts, the native oxides of manganese (*Braunstein*), peroxide of manganese (Bussy & Lecanu); as also by hyponitric acid and sulphate of manganic oxide, but not by nitrites. (Desbassins.)

Sulphate of ferrous oxide is capable of uniting in nearly all proportions with sulphate of zinc-oxide or sulphate of cupric oxide, forming a double salt, of the form of green vitriol.

Sesquisulphate of Ferrous Oxide ?—(For the preparation of this salt, see page 238, β.) Colourless crystals, having a laminar texture like that of gypsum, nearly tasteless, sparingly soluble in water; contain 28·38 p. c. ferrous oxide, 45·42 acid, and 25·97 water—loss 0·33. (Bonsdorff.) Their composition may be nearly represented by $2FeO,3SO^3+7Aq$.

P. Sulphate of Ferric Oxide.—*a. Sexbasic.*—Formed by the weathering of iron pyrites in alum-slate. Dark brown; massive; has a fatty lustre; yields a brownish-yellow powder, and is insoluble in

water, but slowly soluble in heated hydrochloric acid. (Th. Scheerer, *Pogg.* 45, 188.)

	Approximate calculation.				Scheerer.
$6Fe^2O^3$	468	....	78·26	.....	80·73
SO^3	40	....	6·70	.....	6·00
$10HO$	90	....	15·04	.....	13·57
$6Fe^2O^3, SO^3 + 10Aq$	598	....	100·00	.....	100·30

According to Scheerer, it is $2(7Fe^2O^3,SO^3) + 14Aq$.

b. Quadrobasic.—When tersulphate of ferric oxide is precipitated by acetate of baryta, and the remainder of the sulphuric acid removed from the filtrate by a small quantity of baryta-water, light-brown flakes are thrown down, together with the sulphate of baryta, and may be separated from it by levigation; they contain 88·62 per cent. of ferric oxide and 11·38 of sulphuric acid. (Anthon, *Repert.* 81, 237.)

c. Terbasic or Trisulphate.—Precipitated, on boiling a dilute solution of tersulphate of ferric oxide, even when the latter contains sulphate of potash. After drying at 100°, it is a light powder of a deep orange-yellow colour, that colour being lighter, however, as the solution from which the salt is precipitated is more dilute. It loses its water below a red heat, and turns dark brown; at a red heat, it leaves ferric oxide. It is insoluble in water, but dissolves with tolerable facility in acids. (Th. Scheerer, *Pogg.* 44, 453.)

					Scheerer.
$3Fe^2O^3$	234	....	75·49	.....	74·43
SO^3	40	....	12·90	.....	12·69
$4HO$	36	....	11·61	.....	12·80
$3Fe^2O^3, SO^3 + 4Aq$.	310	....	100·00	.....	99·92

According to Scheerer, it is $2(3Fe^2O^3,SO^3) + 9Aq$.

d. Bibasic or Disulphate.—Occurs native, combined with 6 atoms of water, in the form of *Vitriol-ochre.* Precipitated in the hydrated state on mixing the tersulphate with a quantity of ammonia not sufficient for its complete decomposition; also when an aqueous solution of green vitriol is exposed to the air. It is consequently deposited in vitriol and alum works by the action of the air on the mother-liquid of the vitriol or alum; the deposit is called "the cream" (*Schmand*). Yellowish-brown. Gives off its water when heated, and assumes a brown-red colour: when somewhat strongly ignited, it gives off undecomposed sulphuric acid. (Berzelius, *Gilb.* 40, 293.)

	Anhydrous.				Berzelius.		Thomson.
$2Fe^2O^3$	156	....	79·59	.....	79·8	....	80
SO^3	40	....	20·41	.....	20·2	....	20
$2Fe^2O^3, SO^3$	196	....	100·00	.....	100·0	....	100

	Hydrated.				Berzelius.		Soubeiran.
$2Fe^2O^3$	156	....	62·4	.....	62·4	....	59·0
SO^3	40	....	16·0	.....	15·9	....	11·5
$6HO$	54	....	21·6	.....	21·7	....	29·5
$2Fe^2O^3, SO^3 + 6Aq$.	250	....	100·0	.....	100·0	....	100·0

The salt examined by Soubeiran was obtained by precipitating the tersulphate of ferric oxide with carbonate of potash in the cold.

¶ According to Wittstein, the precipitate deposited from a solution

of green vitriol exposed to the air consists, after being dried at 100°, of sesquisulphate of ferric oxide, $2Fe^2O^3,3SO^3+8Aq.$, and not of disulphate, as stated by Berzelius. (*Repert. Pharm.* 3rd series, 1, 185.) ¶

An ochrey stalactite from the alum-slate quarry at Gernsdorf, having the form of a crust, of sp. gr. 1·8, and pale yellowish-grey colour, was found to contain 40·06 p. c. ferric oxide, 6·80 alumina, 11·90 sulphuric acid, 40·13 water, and 0·11 matrix; these numbers give rather more than 2 atoms of base (ferric oxide and alumina together) and 15 atoms of water to 1 atom of sulphuric acid. (Breithaupt & Erdmann, *Schw.* 62, 104.)

e. Monosulphate.—Formed by adding carbonate of potash to tersulphate of ferric oxide as long as the alkali does not occasion permanent turbidity,—and heating the resulting red liquid till the salt separates out. Light reddish-yellow powder. (Soubeiran, *Ann. Chim. Phys.* 44, 329; also *J. Pharm.* 16, 525.)

				Soubeiran.
Fe^2O^3	78		53·79	55·5
SO^3	40		27·59	25·5
3HO	27		18·62	19·0
$Fe^2O^3,SO^3+3Aq.$	145		100·00	100·0

f. Sesquisulphate.—Fibroferrite.—Warty; separates in scales; fibrous in a direction perpendicular to the surface of separation; specific gravity, about 2·5; pale greenish-grey; powder yellowish; fibres translucent. Tastes somewhat rough and sour. When heated, it evolves a large quantity of water with a small quantity of sulphur (inasmuch as the mineral contains 10 per cent. of earthy matter and sulphur), the fibres separating at the same time, and assuming an orange-yellow colour. On charcoal before the blowpipe, it decrepitates violently; emits an odour of sulphur, and leaves ferric oxide. In cold water, it splits into fibres, a small quantity being partially dissolved. Boiling-water takes up rather more, and colours the fibres orange-yellow. In hydrochloric acid it swells up like a sponge; acquires a bright orange-yellow colour, and soon dissolves with the exception of the sulphur and the earthy portions. (Prideaux, *Phil. Mag. J.* 18, 397; also *J. pr. Chem.* 24, 127.)

				Prideaux.	Or:
$2Fe^2O^3$	156		35·62	31	34·44
$3SO^3$	120		27·40	26	28·89
18HO	162		36·98	33	36·67
Earthy matter, Sulphur, and loss				10	
$2Fe^2O^3,3SO^3+18Aq.$	438		100·00	100	100·00

g. Bisulphate.—If to a tolerably concentrated solution of tersulphate of ferric oxide, hydrate or carbonate of lime be added till the precipitate no longer re-dissolves, and the liquid be rapidly filtered, the dark brown filtrate contains the bisulphate. This salt may likewise be obtained by agitating a concentrated solution of the tersulphate with the disulphate precipitated in the cold (that which is precipitated from a hot solution will not dissolve). The quantity of disulphate thus dissolved is not, however, sufficient to convert the whole of the tersulphate into bisulphate. The yellow deposit formed on crystals of green vitriol exposed to the air consists of this same salt; hence the solution in cold water of green vitriol thus altered deposits a large quantity of disulphate when heated.

The solution of the bisulphate, when abandoned to spontaneous eva-

poration, leaves a gummy, yellowish-brown mass. When left to itself, it is partly resolved into disulphate which is precipitated, and tersulphate which remains in solution; the decomposition is, however, less complete as the solution is more concentrated. For complete decomposition, a boiling heat is necessary. This salt forms double salts with the sulphates of potash and ammonia, and expels the tersulphate of ferric oxide from its combinations with these alkaline sulphates. (Maus, *Pogg.* 11, 77.)

					Maus.
Fe^2O^3	78	....	49·37	.....	49·9
$2SO^3$	80	....	50·63	.....	50·1
$Fe^2O^3, 2SO^3$	158	....	100·00	.....	100·0

To this head belongs an iron ore from the province of Coquimbo, in Chili, which occurs in globular deposits of a dingy yellow-green colour, silky lustre, and excentrically fibrous texture. Cold water decomposes it gradually, boiling water more quickly, with separation of ferric oxide [or disulphate ?]. (H. Rose, *Pogg.* 27, 310.)

					H. Rose.		Or:
Fe^2O^3	78	....	31·45	....	28·11	....	31·44
$2SO^3$	80	....	32·26	....	27·82	....	31·12
$10HO$	90	....	36·29	....	33·48	....	37·44
$CaO, SO^3 + 2Aq.$		....		....	5·86		
$MgO, SO^3 + 7Aq.$		....		....	3·63		
SiO^2		....		...	1·43		
$Fe^2O^3, 2SO^3 + 10Aq.$	248	....	100·00	....	100·33	....	100·00

Another ore, from the same locality, occurring in thin six-sided tables, or granular, yellow, and translucent, contains more than 2 and less than 3 atoms of sulphuric acid to 1 atom of ferric oxide, viz. 2·64 p. c. magnesia; 26·11 ferric oxide; 1·95 alumina; 39·60 sulphuric acid; 29·67 water; and 1·37 silica. (H. Rose.)

h. Tersulphate.—The so-called *Neutral Sulphate of Ferric Oxide.*—A solution of green vitriol, exposed to the air, or boiled with nitric acid and freed from that acid by repeated solution and evaporation to dryness, is resolved into disulphate of ferric oxide and soluble tersulphate. If the solution of the ferrous sulphate is previously mixed with half as much sulphuric acid as it already contains, it is wholly converted into ferric tersulphate. The same solution is obtained by treating one of the more basic salts, or the ferric oxide itself, with dilute sulphuric acid, or by treating iron filings or ferrous sulphate with excess of oil of vitriol till the excess is evaporated, and then dissolving in water. 30 lb. of hydrated ferric oxide, 70lb. of red oxide, and 150 lb. oil of vitriol, heated in an iron vessel, rise to a bright red heat, with evolution of sulphuric acid, vapour being evolved, and portions of the mass projected out of the vessel. (Prückner, *Schw.* 66, 296.) The yellowish-brown liquid, which strongly reddens litmus, is converted by evaporation into a brownish-yellow syrup; and this, when kept for some time, solidifies into a partly pale yellow, partly white mass of indistinct crystals. The colourless, regular octohedrons obtained from the solution by Hausmann and Sylvester (*Ann. Phil.* 13, 298 & 460) probably consisted of ammonia iron-alum or potash iron-alum. On further evaporation, there remains a brown resinous mass, which, when completely deprived of its water, is converted into the dirty-white anhydrous salt. The resinous mass is difficult to dry; but if mixed with water while still hot, it solidifies suddenly, and may then be easily dried

at a gentle heat. (Wittstein, *Repert.* 63, 223.) The anhydrous salt is a white powder, which dissolves slowly, and consequently has but a very slight taste; in the state of solution, however, it tastes strongly ferruginous. When somewhat strongly heated, it gives off anhydrous sulphuric acid. It slowly absorbs moisture from the air, and ultimately deliquesces to a brown liquid. It is perfectly insoluble in strong oil of vitriol, by which, indeed, it is precipitated from the concentrated aqueous solution in the form of the white dehydrated salt. The concentrated aqueous solution does not become turbid on boiling; but the more dilute it is, the more turbid does it become, and the lower is the temperature required to produce the turbidity; the deposit consists of the terbasic salt. The solution of 1 pt. of the salt in 100 water begins to show turbidity at 95°, and deposits, on boiling, about one-third of its ferric oxide in the form of tersulphate; with 200 parts of water, these numbers are 70° and $\frac{1}{2}$; with 400 water, 59° and $\frac{3}{4}$; with 800 water, 50 and $\frac{7}{8}$; with 1000 water, 47·5 and $\frac{9}{10}$. (Th. Scheerer, *Pogg.* 44, 453.) When the solution is digested with iron filings, ferrous sulphate is produced; hydrogen gas is, however, evolved at the same time, and a basic salt of ferric oxide precipitated. (Berzelius.) On boiling the solution with silver, sulphate of ferrous oxide and sulphate of silver-oxide are produced; but as the liquid cools, the silver is again precipitated and the ferric salt reproduced. (*Sch.* 94.) The solution mixed with common salt evolves hydrochloric acid at 60°; and if it be evaporated to dryness, and the residue further heated with access of air, chlorine is given off, and sulphate of soda, together with free ferric oxide, left behind. (Schaffhäutl, *Ann. Pharm.* 43, 28.) The salt is likewise soluble in alcohol.

					Thomson, Bussy & Lecanu.
Fe^2O^3	78	....	39·39	.....	40
$3SO^3$	120	....	60·61	.....	60
$Fe^2O^3,3SO^3$	198	....	100·00	.....	100

Coquimbite.—Found together with the two ores of iron described on page 244. *Fig.* 137; $r:\sigma=151°$; cleavage imperfect, parallel to r and σ; fracture conchoidal; colour violet-white. It appears to have been produced by the weathering of iron pyrites. It dissolves in hydrochloric acid, or in cold water, with the exception of the silica; the latter solution deposits a large quantity of ferric oxide on boiling; when left to itself at ordinary temperatures, it yields indistinct crystals. (H. Rose, *Pogg.* 27, 310.)

					H. Rose.		Or:
Fe^2O^3	78	....	27·08	.....	24·11	....	25·24
Al^2O^3		....		.....	0·92	....	0·96
$3SO^3$	120	....	41·67	.....	41·87	....	43·84
$10HO$	90	....	31·25	.....	28·62	....	29·96
$CaO,SO^3+2Aq.$		....		.....	2·24		
$MgO,SO^3+7Aq.$		....		.....	1·97		
SiO^3		....		.....	0·31		
$Fe^2O^3,3SO^3+10Aq.$	288	....	100·00	.....	100·04	....	100·00

Q. Ferrous Sulphocarbonate.—An aqueous solution of sulphocarbonate of calcium yields, with ferrous salts, a clear mixture of a deep wine-red colour, which gradually becomes darker, and ultimately forms a liquid which appears ink-black by reflected light; when the ferrous salt is in excess, part of the compound is deposited in the form of a black powder. (Berzelius.)

R. Ferric Sulphocarbonate.—Ferric salts yield, with aqueous sulphocarbonate of calcium, a deep red precipitate, which retains its colour when dry, and yields an umber-brown powder. When gently heated, it gives off first bisulphide of carbon, then sulphur, and leaves protosulphide of iron. It is insoluble in water. (Berzelius.)

S. Ferrous Hyposulphophosphite. — FeS, PS. Artificial $\frac{1}{2}$-sulphide of iron finely pulverized and heated with protosulphide of phosphorus in a bulb-tube (p. 26), through which a current of hydrogen gas is passed, takes up the sulphide of phosphorus with avidity, and the deep yellow colour of the powder is thereby converted into black. The product is FeS,PS, contaminated with a small quantity of $2FeS,PS^3$. (Berzelius.)

T. Ferrous Sulphophosphite.—$2FeS,PS^3$. Obtained by heating pulverized iron pyrites in the same manner with protosulphide of phosphorus; combination takes place, attended with powerful evolution of heat. After the excess of protosulphide of phosphorus has been distilled off, there remains a lump reddened externally by a deposit of P^2S,PS, deep yellow within, with a faint metallic lustre, and somewhat granular. The compound, when distilled, leaves 2FeS,PS in the form of a black-brown residue, which is not decomposed by hydrochloric acid, but only by boiling aqua-regia. The undecomposed compound is likewise insoluble in boiling hydrochloric acid. In damp air it is slowly decomposed, emitting a faint odour of sulphuretted hydrogen. (Berzelius, *Ann. Pharm.* 46, 256.)

					Berzelius.
2Fe	54·0	....	32·65	.....	33·90
P	31·4	....	18·98	.....	18·12
5S	80·0	....	48·37	.....	47·98
$2FeS,PS^3$	165·4	....	100·00	.....	100·00

U. Phosphosulphate of Ferric Oxide.—*Diadochite.* Resembles iron-cinder in outward appearance; kidney-shaped or stalactitic; separates in scales; fracture conchoidal; brownish-yellow, somewhat translucent; colours the blowpipe flame green, and fuses at the edges, with some intumescence, to a black, slightly magnetic enamel. (Breithaupt, *J. pr. Chem.* 10, 503; Plattner, *Rammelsberg. Handwörterb. d. Min.* Suppl. 1, 45.) Boiling-water extracts from the pulverized mineral 12·6 p. c. sulphuric acid, without any ferric oxide; 2·3 p. c. acid remains behind. (Rammelsberg, *loc. cit.*) It appears to be: $(Fe^2O^3,2PO^5+8Aq.)+4(Fe^2O^3,SO^3+6Aq)$.

	Diadochite.				Plattner.
$5Fe^2O^3$	390·0	....	39·77	.....	39·69
$2PO^5$	142·8	....	14·56	.....	14·81
$4SO^3$	160·0	....	16·31	.....	15·15
32HO	288·0	....	29·36	.....	30·35
	980·8	....	100·00	.....	100·00

Iron and Selenium.

A. Selenide of Iron.—Vapours of selenium passed over heated iron filings combine therewith, producing considerable evolution of light and heat; when iron filings are heated with pulverized selenium, partial

combination takes place, unattended with visible combustion. Yellowish-grey, with metallic lustre; hard, brittle, with granular fracture; when heated alone, it does not fuse, but merely bakes together. Fuses before the blowpipe, giving off suboxide of selenium, and forming a black, brittle globule, which has a conchoidal fracture, and appears to consist of ferrous selenite. Dissolves in hydrochloric acid, with evolution of seleniuretted hydrogen gas. If the hydrochloric acid contains air, or if the air has access to the liquid, a red cloud is formed, arising from the separation of selenium; at the same time there is evolved another gas which has a very disagreeable odour, is not absorbed by water or by aqueous alkalis, and gives a black precipitate with nitrate of mercurous oxide.

Pounded selenide of iron, when heated with free selenium, takes up an additional quantity, and is converted into a brownish powder, which is insoluble in hydrochloric acid, and gives off the excess of selenium at a strong red heat. (Berzelius.)

B. Selenite of Ferrous Oxide, or Ferrous Selenite.—Iron is scarcely attacked by selenious acid, but becomes covered with a copper-coloured film of selenium.—*a. Monoselenite.* Formed by double affinity. White precipitate, which, when exposed to the air, first turns grey, and then yellow. When freshly precipitated, it dissolves in hydrochloric acid—the solution containing ferric oxide and selenious acid, and a portion of the selenium being separated.

b. Biselenite.—By dissolving *a* in selenious acid, from which, however, it is soon deposited. Slightly soluble in water; the solution, when heated, yields a brown precipitate, which is a mixture of selenium and ferric selenite. (Berzelius.)

C. Selenite of Ferric Oxide, or Ferric Selenite.—*a. Sesquiselenite.*—By digesting *b* or *c* in ammonia. Does not dissolve in water, but passes with it through the filter. Contains about 48 ferric oxide to 52 acid; the latter is completely evolved on the application of heat.

b. Terselenite.—By double decomposition. White powder, becoming somewhat yellowish when dry. When heated, it gives off water, turns red, and loses all its acid. According to Muspratt, it contains 4 atoms of water.

c. Sexselenite.—When iron is dissolved in excess of a mixture of boiling nitric acid and selenious acid, this salt crystallizes on cooling in pistaccio-green laminæ, which give off their water and turn black when heated, afterwards become red on cooling, and give off all their selenious acid, leaving sesquioxide of iron. It is insoluble in water, but dissolves in hydrochloric acid, forming an orange-yellow solution. (Berzelius.)

Iron and Iodine.

A. Protiodide of Iron, or Ferrous Iodide.—1. The two substances unite readily, with slight evolution of heat, and form a brown mass which fuses at a red-heat and volatilizes at a higher temperature. (Guy-Lussac, H. Davy.)—2. Serullas, by passing iodine vapour and vapour of water through a red-hot gun-barrel containing charcoal, obtained highly lustrous crystals which looked like gold filings and contained iodine and iron.—3. When 1 part of iron is digested in water with 2 parts

of iodine and the resulting aqueous iodide of iron boiled down in a glass flask in which an iron wire is placed, a steel-grey mass is obtained, having a laminar fracture, fusing at 177°, of sharp and astringent taste, and smelling of iodine while yet moist. When strongly heated in the air, it gives off iodine in vapour, and is converted into ferric oxide. (Todd Thomson.)

Hydrated Protiodide of Iron, or *Hydriodate of Ferrous Oxide.*—The aqueous solution evaporated in the water-bath yields dark greenish-brown rhombic crystals, which, when strongly heated in the air, give off water and iodine and leave sesquioxide of iron. (J. D. Smith, *Phil. Mag. J.* 7, 156; also *N. Br. Arch.* 5, 56.) The aqueous solution concentrated in a retort till it froths up and attains the consistence of oil, solidifies to a greenish-black crystalline mass, consisting of green crystals which pass to a higher state of oxidation even when kept in air-tight but not exhausted vessels. (Kerner, *Ann. Pharm.* 29, 183.)—The crystalline mass is greyish-black, radiating, and yields a bluish-green powder, which, when kept for 4 months in a stoppered bottle, becomes covered with laminæ of iodine, and afterwards dissolves but partially in water, forming a black-brown solution, while ferric oxide remains undissolved. (Preuss, *Ann. Pharm.* 29, 329.)

Anhydrous.				*Crystallized.*				Smith.
Fe	27	....	17·65	Fe	27	....	13·64	.... 14·14
I	126	....	82·35	I	126	....	63·64	.... 63·64
				5HO	45	....	22·72	.... 22·22
FeI	153	....	100·00	+5Aq.	198	....	100·00	.... 100·00

Aqueous Protiodide of Iron, or *Aqueous Hydriodate of Ferrous Oxide.*—When 1 part of iron is brought in contact with 2 or 3 parts of iodine and with water, heat is evolved and a pale bluish-green solution formed. This liquid rapidly absorbs the oxygen of the air, with formation of ferric oxide—whereby a small quantity of basic salt is deposited—and evolution of iodine. This tendency to oxidation may be almost wholly prevented by adding sugar in quantity equal to twice that of the iodine, and evaporating to the consistence of syrup. (Frederking.)

There appears to be no *Sesqui-iodide of Iron*, or *Terhydriodate of Ferric Oxide.*

1. When 2 parts of iodine diffused through water are saturated with iron, and 1 part more of iron added to the pale green filtrate (which is capable of taking up more than 1 pt.) there is produced a dark red-brown mixture, which smells strongly of iodine, and is probably a mere solution of iodine in aqueous protiodide of iron [hydriodite of ferrous oxide]; it exhibits the reactions of a ferrous salt: Green precipitate with caustic alkalis and green with alkaline carbonates, soon turning red-brown; no colouring with sulphocyanide of potassium (but on the addition of sesqui-chloride of iron, the red colour immediately appears); blue with starch; and nevertheless a blue precipitate with ferrocyanide of potassium. The mixture when evaporated gives off iodine and leaves a brown-red mass. (Kerner, *Ann. Pharm.* 30, 117.)—The precipitate formed by ferrocyanide of potassium is light blue at first and afterwards [in consequence of the free iodine?] becomes dark blue. Ferricyanide of potassium gives immediately a dark blue precipitate. The solution evaporated to the consistence of syrup, whereby iodine is evolved, crystallizes on cooling in very deliquescent red-brown needles, from which water extracts protiodide of iron containing excess of iodine, and leaves ferric oxide. (Oberdörffer,

N. Br. Arch. 22, 296.)—2. Aqueous hydriodic acid prepared from 126 parts of iodine, when gently heated with excess of recently precipitated hydrate of ferric oxide, dissolves a quantity corresponding to 62·56 parts of the anhydrous oxide. The solution smells of iodine and exhibits the reactions mentioned under (1); hence it would appear that part of the ferric oxide and the hydriodic acid decompose each other, yielding protiodide of iron, free iodine, and water. (Kerner.) [The quantity of ferric oxide which Kerner found to be dissolved, is too great to correspond with the formula: $Fe^2O^3+3HI=2FeI+I+3HO$.]—The yellowish-red solution of ferric oxide in aqueous hydriodic acid is partly resolved by heat into protiodide of iron and free iodide. (Lassaigne, *J. Chim. méd.* 5, 333.)—3. Aqueous protiodide of iron deposits ferric oxide when exposed to the air; the remaining liquid, however, contains no sesqui-iodide of iron, but (to judge by its reactions with alkalis) protiodide of iron and free iodine. (P. Squire, *Phil. Mag. J.* 9, 79.)

According to Berzelius, the brown powder which is deposited on exposing aqueous protiodide of iron to the air, is not pure ferric oxide, but a basic salt.

B. *Iodate of Ferrous Oxide*, or *Ferrous Iodate?*—Iron dissolves without effervescence in iodic acid either dilute or concentrated; when the solution is boiled, a white powder is precipitated. (A. Connell, *N. Edinb. Phil. J.* 11, 72.)—Iodate of potash gives a yellowish-white precipitate with solution of green vitriol. (Pleischl.) The precipitate is soluble in excess of solution of green vitriol; hence, it is only on the addition of considerable quantities of iodate of potash, that the precipitate, which is of a dingy flesh-colour, becomes permanent. It has an astringent, ferruginous taste. It dissolves sparingly in water, readily in solution of green vitriol; the latter solution, when boiled, deposits basic iodate of ferric oxide, iodine being set free at the same time. (Geiger, *Mag. Pharm.* 29, 253.)—The precipitate which iodate of potash yields with green vitriol is white at first, but soon turns yellow, giving off iodine and increasing in quantity, and afterwards changes to brown basic iodate of ferric oxide. The mother-liquid, which has a yellow colour, deposits an additional quantity on boiling, and is afterwards found to contain free hydriodic acid. (Rammelsberg, *Pogg.* 44, 559.)—With hydrochlorate of ferrous oxide iodate of potash gives a white precipitate, which when heated gives off chlorine and turns brown. (Simon.)

C. Iodate of Ferric Oxide.—*a. Basic Salt.*—Precipitated, on heating a mixture of iodate of potash and green vitriol, in the form of a yellowish-brown powder, having an astringent, ferruginous taste. When heated in contact with paper, it detonates and gives off iodine vapour. (Geiger.)—The light brown precipitate which forms when the mixture is left to stand in the cold for some time, dissolves in hydrochloric acid with rapid evolution of chlorine, whereupon ammonia throws down a mixture of hydrated ferric oxide and iodide of nitrogen, which detonates violently when dry. Dissolves readily in nitric acid, forming a liquid which contains no hydriodic acid, since it gives with nitrate of silver-oxide a copious precipitate perfectly soluble in ammonia. The light brown precipitate contains 19·28 per cent. of ferric oxide, 70·73 iodic acid, and 9·99 water; it is therefore $3Fe^2O^3,5IO^5+15Aq$. (Rammelsberg.) [The formula $4Fe^2O^3,7IO^5+18Aq$. corresponds still more closely with the analysis; but both these formulæ are improbable.]

b. Biniodate.—Iodic acid and iodate of potash form with hydrochlorate of ferric oxide a white precipitate soluble in excess of the ferric hydrochlorate. (Pleischl.) This precipitate, after washing and drying, has a dirty white colour and a weak ferruginous taste; is resolved by heat into iodine vapour and ferric oxide; deflagrates with a violet light when heated with charcoal powder; dissolves readily in hydrochlorate of ferric oxide and in 500 parts of cold water. The latter solution is colourless, but turns slightly brown when heated and deposits a few flakes. (Geiger.)—The precipitate obtained with iodate of soda and sulphate of ferric oxide and ammonia is yellowish-white, with a tinge of red after drying; is resolved at a red-heat into oxygen gas, iodine vapour and ferric oxide; and is sparingly soluble in nitric acid. (Rammelsberg.)

					Rammelsberg.
Fe^2O^3	78	....	16·18	....	15·92
$2IO^5$	332	....	68·88	....	69·37
8HO	72	....	14·94	....	14·71
$Fe^2O^3,2IO^5+8Aq.$	482	....	100·00	....	100·00

D. and E. Ferrous and Ferric Periodates.—Mono-iodate of soda gives with ferrous and also with ferric salts, yellowish-white precipitates soluble in dilute nitric acid. (Benckiser, *Ann. Pharm.* 17, 260.)

Iron and Bromine.

A. Protobromide of Iron, or Ferrous Bromide.—Bromine does not act upon iron in the cold. (Berthemot.)—1. When bromine vapour is passed over gently ignited iron wire, the wire glows vividly, fuses, and is converted into yellowish protobromide of iron. (Liebig, *Schw.* 48, 107.)—Iron filings similarly treated bake together into a greyish mass covered with golden-yellow scales of [sesqui?] bromide of iron which may be sublimed. (Berthemot, *Ann. Chim. Phys.* 44, 391; also *J. Pharm.* 16, 657.)—2. When iron filings are heated with hydrobromate of ammonia, hydrogen gas and ammonia are evolved, and bromide of iron in a very difficultly fusible state remains behind. (Löwig.)—3. A solution of iron in bromine and water, the iron being in excess, leaves dry bromide of iron when evaporated. (Berthemot.)—Protobromide of iron, when ignited in the air, yields a sublimate of sesquibromide of iron, while sesquioxide remains behind. (Löwig.)

Aqueous Protobromide of Iron, or *Hydrobromate of Ferrous Oxide.*—When bromide of iron is dissolved in water, or when iron is dissolved in a mixture of bromine and water, or in aqueous hydrobromic acid, a pale green solution is obtained, which, when cooled after evaporation, yields rhombic tables of sex-hydrated bromide of iron, and when exposed to the air turns brown and deposits ferric oxybromide. (Löwig.)

	Anhydrous.				Berthemot.				
Fe	27·0	....	25·62	....	26·04	Fe	27·0	....	16·94
Br	78·4	....	74·38	....	73·96	Br	78·4	....	49·18
						6HO	54·0	....	33·88
FeBr	105·4	....	100·00	....	100·00	+6Aq.	159·4	....	100·00

B. Sesquibromide of Iron, or Ferric Bromide.—1. By heating the *protobromide* with bromine. (Löwig.)—2. By evaporating to dryness a

solution of iron in excess of bromine-water. (Liebig.—Brown-red; fuses at a gentle heat; while, at a higher temperature, part of it sublimes in laminæ resembling mosaic gold, and the rest is resolved into vapour of bromine and a residue of ferrous bromide. (Löwig.)

Aqueous Sesquibromide of Iron, or *Hydrobromate of Ferric Oxide.*—Sesquibromide of iron deliquesces when exposed to the air. (Liebig.)—The same solution is obtained by dissolving hydrated ferric oxide in aqueous hydrobromic acid, or by mixing aqueous protobromide of iron with bromine. The solution, which is of a yellowish-brown colour, much darker than that of the sesquichloride, and has a strongly ferruginous taste, gives off hydrobromic acid when evaporated, and deposits the following compound. It does not yield crystals when concentrated to the consistence of a syrup; but when completely evaporated, leaves a brown-red mixture of the following compound and sesquibromide of iron, which latter may be sublimed by heat. (Löwig.)

C. Ferric Oxybromide.—A compound of sesquioxide of iron with the sesquibromide.—Precipitated on evaporating the aqueous solution of sesquibromide of iron, or on mixing it with an insufficient quantity of potash-ley, or on exposing aqueous protobromide of iron to the air. (Löwig.)

Bromine-water converts hydrated ferrous oxide into hydrated ferric oxide and bromide of iron, which dissolves; not a trace of ferric oxide is taken up. (Balard.)

Bromate of Ferrous Oxide does not appear to exist. Green vitriol yields with bromate of potash a brown-red precipitate, which dissolves in a larger quantity of water, forming a brown-red solution. (Löwig.) This precipitate consists of basic sulphate of ferric oxide, and the liquid contains free bromine. (Rammelsberg.) Bromate of potash yields, with hydrochlorate of ferrous oxide, without precipitation, a darker mixture, which acquires a dark brown colour when heated. (Simon.)

D. Bromate of Ferric Oxide, or Ferric Bromate.—Recently precipitated hydrate of ferric oxide yields, with aqueous bromic acid, a reddish-yellow solution, which, when evaporated over oil of vitriol in a receiver filled with air, acquires a greenish tinge, and without yielding crystals, forms a syrup, and afterwards, on evaporation over the water-bath, a dark brown mass, from which water dissolves out the smaller portion, forming a yellowish solution, while the greater part remains undissolved in the form of a *quintobasic salt*. This, when ignited, evolves water, oxygen gas, and bromine vapour, and leaves black ferric oxide; it dissolves in nitric acid. (Rammelsberg, *Pogg.* 55, 68.)

				Rammelsberg.
$5Fe^2O^3$	390·0	50·10		50·89
BrO^5	118·4	15·21		
$30HO$	270·0	34·69		33·73
$5Fe^2O^3,BrO^5+30Aq.$	778·4	100·00		

Iron and Chlorine.

Protochloride of Iron, or Ferrous Chloride.—1. Formed by boiling down a solution of iron in hydrochloric acid out of contact of air, and heating the residue till the water is expelled. The heating may be

performed in a glass tube closed at one end, and drawn out to a fine point at the other; or in a stream of hydrogen gas.—2. By passing chlorine gas through a red-hot gun-barrel filled with iron turnings, the barrel being connected immediately at the part which projects from the furnace, with a receiver in which the chloride of iron sublimes.—3. By passing hydrochloric acid gas over red-hot iron filings.—4. When iron filings are heated with sal-ammoniac, protochloride of iron remains in the residue.

When prepared by method (1), it is white (Chevreul), without metallic lustre, opaque, and has a laminar fracture; fuses at a red heat, but does not volatilize even at the melting point of glass. (J. Davy, *Schw.* 10, 326.) —By (2), small white scales are obtained. (Thénard, *Traité.*)—By (3), white micaceous scales. (Wöhler & Liebig, *Pogg.* 21, 582.)—By (4), Pagenstecher (*N. Tr.* 3, 1, 399) obtained a mass consisting of soft, white, silky laminæ, which dissolved in water without evolution of heat, and formed a colourless liquid, which turned green in the air, and gave a black precipitate with ammonia.

					J. Davy.
Fe	27·0	....	43·27	.....	46·57
Cl	35·4	....	56·73	.....	53·43
FeCl	62·4	....	100·00	.....	100·00

Decomposed by ignition in a stream of oxygen gas or with chlorate of potash, yielding ferric oxide and chlorine. (Gay-Lussac.) When heated with moderate excess of air, it gives up one-third of its iron to the oxygen, and is converted into sesquichloride of iron which sublimes, and sesquioxide which remains behind:

$$6FeCl + 3O = 2Fe^2Cl^3 + Fe^2O^3.$$

When brought in contact with vapour of water at a red heat, it gives off hydrochloric acid and hydrogen gas, and is converted into ferroso-ferric oxide. (Gay-Lussac, *Ann. Chim. Phys.* 22, 424.)

$$3FeCl + 4HO = Fe^3O^4 + 3HCl + H.$$

With phosphuretted hydrogen gas, even at ordinary temperatures, it forms hydrochloric acid gas and phosphide of iron. (H. Rose, *Pogg.* 24, 301.)—Oil of vitriol decomposes it, even when cold, the products being hydrochloric acid gas and ferrous sulphate. (A. Vogel.) Does not yield sulphide of iron when ignited with sulphur. (A. Vogel.)

Tetra-hydrated Protochloride of Iron, or *Ter-hydrated Hydrochlorate of Ferrous Oxide.*—Formed by evaporating and cooling a saturated solution of iron in hydrochloric acid out of contact of air.—Hydrochloric acid is boiled with excess of iron in a narrow-necked flask, till it is thoroughly saturated and sufficiently concentrated; the liquid thereby acquires a brownish-grey colour, and often, towards the end of the operation, becomes pale grey from formation of a basic ferrous salt, and exhibits a tendency to frothing; hence the heat must be kept moderate towards the close of the process. The solution is then—as in the preparation of green vitriol—passed through a filter moistened with water, the filter being placed in a funnel having a long neck which reaches to the bottom of a vessel previously rinsed out with hydrochloric acid. The resulting crystals are exposed to sunshine at a temperature between 30° and 40°, and constantly turned till they are dry; they are then preserved in stoppered bottles. They keep best when they have been dried at 50°: at that temperature, however, they effloresce slightly. (v. Bonsdorff, *Pogg.* 31, 89.)—Light

blue, translucent, oblique rhombic prisms, truncated on the acute lateral edges (*Fig.* 87), without the *i*- and *h*-faces; often shortened into tables. (Bonsdorff.) Pale green, broadly truncated rhombic octohedrons, or rhombic prisms acuminated with octohedral faces. (*Figs.* 42 and 44; Reimann, *Mag. Pharm.* 17, 215.)—In ordinary air, the crystals soon acquire a grass-green colour; in air dried by oil of vitriol, they quickly effloresce to a white powder. (Bonsdorff.) When heated, they fuse in their water of crystallization. (Reimann.)

When iron is dissolved in strong hydrochloric acid, crystals are formed at a certain stage of the operation, which dissolve in water with decrepitation and evolution of an inflammable gas. (Hess, *J. pr. Chem.* 25, 126):

	Crystallized.				Bonsdorff.		Reimann.
Fe	27·0	....	27·44	.....	63·95	....	33·33
Cl	35·4	....	35·98				
4HO	36·0	....	36·58	.....	36·05		
FeCl + 4Aq	98·4	....	100·00	.....	100·00		

According to Graham, also (*Ann. Pharm.* 29, 31) the crystals contain 4 At. water to 1 At. chloride of iron.

Protochloride of iron, whether dry or hydrated, deliquesces rapidly in the air and dissolves readily in water and alcohol; 1 part of the hydrated salt requires 0·68 cold water to dissolve it. (Reimann.)

The aqueous solution of protochloride of iron—in the same manner as green vitriol—absorbs $\frac{1}{4}$ At. nitric oxide gas, and thereby acquires a dark greenish-brown colour. 249·6 pts. (4 At.) protochloride of iron dissolved in either a large or a small quantity of water, absorbs 25·14 pts. of nitric oxide, and the mixture exhibits the same relations as that obtained with green vitriol.—Dry protochloride of iron likewise absorbs a small quantity of nitric oxide, and becomes dark-coloured. 100 parts of dry protochloride of iron absorb from 2 to 3·66 parts of perfectly dry nitric oxide gas. (Graham.)—A much larger quantity is absorbed by the solution of dry protochloride of iron in absolute alcohol, which thereupon becomes nearly black. A solution of 1 pt. chloride of iron in 5 pts. alcohol saturated with nitric oxide, evolves a portion of that gas when heated, boils at 100°, giving off the remainder of the nitric oxide in its original state, the volume of the gas evolved being 23 times that of the alcohol; after several hours' boiling, the liquid regains the colour which it had before saturation with the gas. (Graham, *Phil. Mag. Ann.* 4, 265 & 331; also *Schw.* 55, 200.)

B. Sesquichloride of Iron, or Ferric Chloride.—*Perchloride of Iron; Iron Sublimate.*—1. A piece of iron wire or a watch-spring introduced red-hot, or with a piece of burning tinder at the end, into chlorine gas, burns with a red glow and forms this compound, which then sublimes. The same result may be obtained by passing chlorine gas over gently heated iron.—2. Protochloride of iron heated in chlorine gas, is converted into the sesquichloride.—3. When protochloride of iron is heated in a vessel containing air, sesquichloride sublimes, and sesquioxide remains behind.—4. When an aqueous solution of the sesquichloride is evaporated, the dry compound remains behind, mixed with more or less ferric oxychloride; the dry residue gently ignited in a loosely closed flask, yields the sesquichloride sublimed in laminæ.—5. A mixture of 1 pt. calcined ferrous sulphate, and 1 pt. chloride of calcium, is ignited in a flask till the

ferric chloride sublimes. (Baur, *Repert*, 25, 432.)—Iron-black, iridescent tables, having a metallic lustre, and volatilizing and subliming somewhat above 100°.

					J. Davy.
2Fe	54·0	....	33·71	.....	35·1
3Cl	106·2	....	66·29	.....	64·9
Fe^2,Cl^3	160·2	....	100·00	.....	100·0

When heated in contact with oxygen gas, it yields ferric oxide and chlorine; heated with aqueous vapour, it forms ferric oxide and hydrochloric acid gas. With oil of vitriol and with sulphur, it behaves like the protochloride. (A. Vogel.)

Hydrated Sesquichloride of Iron, or *Hydrochlorate of Ferric Oxide.*—Sesquichloride of iron dissolves in water with considerable evolution of heat, and likewises deliquesces in the air. The liquid formed by deliquescence is called *Oleum Martis.* The same solution may be obtained by the following methods: 1. By dissolving ferric oxide or its hydrate in boiling hydrochloric acid. Pure blood-stone finely pounded may likewise be used for this purpose. (Mohr.) 2. By dissolving iron to saturation in a definite quantity of hydrochloric acid; filtering the solution, and mixing it with half as much hydrochloric acid as it already contains; then heating the liquid to ebullition in a capacious vessel, and adding nitric acid in small portions till the dark brown colour first produced by the absorption of nitrous gas has given place to a yellowish-brown, and the further addition of nitric acid produces no evolution of nitrous gas. The mixture is very apt to froth over, especially towards the end of the operation, when all the nitric oxide which has been absorbed is evolved. The same result may also be obtained by dissolving iron in aqua-regia; but it is not easy to hit the right proportion of the acids.—3. By passing washed chlorine gas through aqueous hydrochloric acid saturated with iron, as long as the gas is absorbed. The dark brown liquid, which has a rough taste and colours the skin yellow, yields, on evaporation and cooling, crystals containing two different proportions of water.

a. Penta-hydrated.—1. Obtained by evaporating the liquid to a syrup—mixing it with a small quantity of strong hydrochloric acid to re-dissolve the precipitated ferric oxychloride—and leaving it to itself in the cold. (Stein, *Repert.* 13, 264.)—2. By fusing the crystals *b*—evaporating till the liquid becomes perfectly solid on cooling—replacing the lost hydrochloric acid—and leaving the solution to cool. (Fritzsche.)—3. The crystals *b*, placed beside oil of vitriol under a receiver containing air, soon deliquesce and form a thick liquid, in which large crystals then form, till the whole is converted into a mass of crystals. (Fritzsche, *J. pr. Chem.* 18, 479.) Aurora-red tables (Stein); large, deep, reddish-yellow crystals, which fuse readily, and solidify again at 42°; they absorb water from the air very rapidly, and with evolution of heat. (Fritzsche.)

					Fritzsche (*mean.*)
2Fe	54·0	....	26·32	.....	27·12
3Cl	106·2	....	51·75	.....	50·72
5HO	45·0	....	21·93	.....	21·86
$Fe^2Cl^3 + 5Aq.$	205·2	....	100·00	.....	100·00

When the crystals *a* and *b* are shaken together, a slight fall of temperature takes place, and a liquid is obtained—the same as that produced by

imperfect evaporation of the crystals *b*—which produces great heat when mixed with water. (Fritzsche.) 1 At. ferric chloride dissolved in 9 At. water yields a liquid, which is identical with the *Oleum Martis* of the older chemists (as obtained by deliquescence of the solid chloride in the air), has a density of 1·545, and refuses to crystallize. (Kinast.) Hence there are two solutions of ferric chloride in water to be distinguished; one containing more than 5 and less than 12 atoms of water, the other containing more than 12 atoms.

b. Dodeca-hydrated.—Ferric chloride deliquesces rapidly in the air, then crystallizes in the form of this salt, and afterwards deliquesces much less quickly. (Kinast, *Kastn. Arch.* 20, 281.) This salt likewise separates slowly from an aqueous solution of the chloride not too much concentrated —fine radii stretching out in all directions from particular points, and forming pale orange-yellow, opaque, hemispheric nodules, into which the whole liquid is ultimately converted. If the evaporation has been carried too far, the syrup will not crystallize unless it be exposed for some time to the damp air of a cellar, from which it can absorb water. (Mohr, *Ann. Pharm.* 29, 173.) A crystalline mass of this nature, having been kept for half a year in a stoppered bottle, was found to be converted into brown-red transparent rhombic tables [of salt *a* ?], surrounded by a small quantity of liquid. (Winckler, *Repert.* 67, 150.)

			Fritzsche (*mean.*)	Mohr.
2Fe	54·0	20·13	21·57	20·59
3Cl	106·2	39·60	39·07	39·23
12HO	108·0	40·27	39·36	40·18
$Fe^2Cl^3 + 12Aq.$	268·2	100·00	100·00	100·00

Aqueous Sesquichloride of Iron, or *Aqueous Terhydrochlorate of Ferric Oxide.* The salt *b* deliquesces slowly in the air. The aqueous solution, when evaporated, gives off more or less hydrochloric acid, depositing ferric oxychloride; and if evaporated to perfect dryness—whereupon a further quantity of acid, together with some ferric chloride, is given off—it leaves a mixture of ferric chloride with ferric oxychloride. When silver is immersed in the solution, protochloride of iron is formed, and the silver is converted into chloride, which is black at first, but afterwards turns white. (Wetzlar.)

Ferric chloride is likewise soluble in alcohol and in ether; but if exposed to light or heat, it is converted, especially by the ether, into protochloride. The solution of ferric chloride in a small quantity of alcohol of 96 per cent., remains liquid at 7·5°; but, if stirred with a glass rod, immediately solidifies to a solid yellow crystalline mass, whereupon the temperature rises to + 19°. (Winckler.)

C. Ferric Oxychloride, or Basic Hydrochlorate of Ferric Oxide.—*a. Soluble Compound.*—When recently precipitated hydrate of ferric oxide is added to an aqueous solution of ferric chloride, as long as it dissolves, a dark red liquid is obtained, having a specific gravity of 1·017. This liquid does not become turbid on boiling, dilution, or evaporation to dryness; but if mixed with a few drops of nitric acid, it deposits the greater part of the oxide in the form of a basic compound, and gives a dark bluish-green precipitate with ferrocyanide of potassium. A sample of this liquid yielded by precipitation with potash, 155 parts of ferric oxide, and afterwards by precipitation with nitrate of silver (after addition

of nitric acid) 60 parts of chloride of silver. [Hence this compound appears to consist of $14Fe^2O^3 + Fe^2Cl^3$.] If more hydrated oxide be added to the liquid than it is able to take up, the soluble compound unites with it, and forms the insoluble variety. (Phillips, *Phil. Mag. Ann.* 8, 406; also *Br. Arch.* 39, 39.)

b. Insoluble Compound. — Precipitated in rust-brown flakes when hydrochlorate of ferric oxide is mixed with an insufficient quantity of an alkali, or when it is evaporated, or when the mono-hydrochlorate of ferrous oxide is exposed to air in the hydrated state. When heated it first gives off water, then ferric chloride, and leaves ferric oxide.

Hypochlorite of Ferric Oxide does not appear to exist. Hydrated ferric oxide dried in the air, and then introduced into dry chlorine gas, quickly fuses into a dark red liquid, which decolorizes indigo and gives off all its chlorine at a boiling heat, leaving ferric oxide. (Grouvelle.) The absorption goes on slowly; the solution exerts a decolorizing action, evolves chlorine and hypochlorous acid when heated, and deposits the ferric oxide. It appears to consist of sesquichloride of iron and free hypochlorous acid, which, on the application of heat, are resolved into free chlorine and ferric oxide. Aqueous hypochlorous acid does not dissolve ferric oxide; and when hypochlorite of lime is mixed with ferric sulphate, the ferric oxide is precipitated together with the sulphate of lime, and free hypochlorous acid remains in the liquid. (Balard.)

D. Perchlorate of Ferrous Oxide, or Ferrous Perchlorate.— When green vitriol is precipitated by perchlorate of baryta, and the liquid filtered and evaporated, long colourless needles are obtained, which remain permanent for a long time in the air, and then oxidize in the manner of green vitriol. They scarcely detonate on glowing coals. When the solution is evaporated in the air, a small quantity of ferric salt is formed. (Serullas, *Ann. Chim. Phys.* 46, 305.)

Iron and Fluorine.

A. Protofluoride of Iron, FeF, and Monohydrofluate of Ferrous Oxide.—Iron dissolves in warm aqueous hydrofluoric acid, with evolution of hydrogen. The liquid, when evaporated, yields white rectangular tables, which turn pale yellow in the air. These crystals, when gently heated, give off water, and are converted into the dry protofluoride of iron, which undergoes no alteration when ignited in the air; but if the crystals are suddenly heated, a small quantity of hydrofluoric acid goes off together with the water, and the residue has a red tinge from admixture of ferric oxide. The crystals dissolve with difficulty in pure water —more easily in water containing hydrofluoric acid. Alkalis precipitate hydrated ferrous oxide from the solution. Protofluoride of iron combines with the fluorides of the alkali-metals, forming colourless, difficultly fusible compounds. (Berzelius.)

B. Sesquifluoride of Iron, Fe^2F^3, and Ter-hydrofluate of Ferric Oxide.—Formed by saturating aqueous hydrofluoric acid with hydrated ferric oxide. The colourless solution, when evaporated, deposits pale flesh-coloured crystals, having a sweet and rough taste. These crystals re-dissolve perfectly, but slowly, in water, forming a colourless

liquid. Sesquifluoride of iron combines with other metallic fluorides, forming compounds which, for the most part, are nearly or quite insoluble, but nevertheless are not deposited from a mixture of the aqueous solutions of the two fluorides till heat is applied. (Berzelius.)

C. Ferric Oxyfluoride, or Basic Hydrofluate of Ferric Oxide. Precipitated on mixing the aqueous solution of B with excess of ammonia. Rusty-yellow powder. (Berzelius.)

Iron and Nitrogen.

A. Nitride of Iron.—Dry ammoniacal gas passed over iron wire heated to redness in a tube, is resolved into hydrogen and nitrogen gases, and the iron becomes very brittle, though it does not perceptibly increase in weight. (A. Berthollet, *Gilb.* 30, 378.) The increase in weight, after the gas has been passed over the iron for 24 hours, does not exceed 0·2 pts. for 100 parts of the iron. (Thénard, *Ann. Chim.* 85, 61; also *Gilb.* 46, 267.) After 9 hours' passage of the gas, it amounts to only 0·15 to every 100 parts of iron; after 2 hours' passage of the gas, the iron appears brittle, exhibits the fine-grained fracture of steel, may be hardened in the same manner as steel, and will then give sparks with flint; but after 9 hours' passage of the gas, it is even softer than common iron, no longer admits of hardening, and its specific gravity is diminished from 7·788 to 7·6637. (Savart, *Ann. Chim. Phys.* 37, 326; also *Pogg.* 13, 172.) —When ammoniacal gas, freed from water and carbonic acid by passing over chloride of calcium and hydrate of potash, is passed for 6 or 8 hours over red-hot iron, 100 parts of the iron increase in weight by 7 to 11·5 pts. [11·5 : 100=14 : 121·7; hence each atom of nitrogen is united with more than 4 At. (108 pts.) and less than 5 At. (135 pts.) of iron]. The nitride of iron thus obtained is white, brittle, and even friable; its specific gravity often does not exceed 5·0; with the magnet and with acids it acts like other iron, but is more readily altered by air and water.—Hydrogen gas, passed over red-hot nitride of iron, withdraws the nitrogen from it and forms ammonia; a case of reciprocal affinity. The hydrogen gas evolved when nitride of iron is dissolved in dilute sulphuric acid contains about 6 per cent. of nitrogen; the quantity of gas evolved is also less than when pure iron is used, because sulphate of ammonia is formed at the same time. Sometimes the iron, after ignition in ammoniacal gas, is found to be altered in its physical properties, as above described, and yet has not increased in weight; in such a case, the combination of the nitrogen with the iron is but transient, but has the effect of altering the mutual arrangement of the atoms. (Despretz, *Ann. Chim. Phys.* 42, 122; also *Pogg.* 17, 296.)

B. Nitrate of Ferrous Oxide, or Ferrous Nitrate.—*Protonitrate of Iron.*—1. Formed by precipitating nitrate of baryta with an equivalent quantity of ferrous sulphate and evaporating the filtrate in vacuo over oil of vitriol.—2. By dissolving iron in very dilute nitric acid, and exposing the solution to the air to free it from nitric oxide, which gives it a greenish-brown colour. (H. Davy.)—The iron should be immersed in water, and nitric acid free from nitrous acid and chlorine, added in small portions and with constant agitation, so that the temperature may not rise above 50°; as often as the liquid cools down, fresh acid must be

added. Under these circumstances, no gas is evolved, but nitrate of ammonia is formed at the same time. (Berzelius.)

$$8Fe + 10NO^5 + 3HO = 8(FeO,NO^5) + NH^3,NO^5.$$

1 part of nitric acid with 3 parts water evolves no gas in acting upon iron; with 2 parts water, nitrous oxide is at first evolved, mixed with nitric oxide; afterwards only the latter. (Pleischl, *Schw.* 38, 464.)—The pale green solution thus obtained does not deposit ferric oxide or give off nitric oxide gas, till it is heated to the boiling point. (Berzelius, *Pogg.* 27, 121.)—3. Protosulphide of iron dissolves in dilute nitric acid surrounded with a frigorific mixture, hydrosulphuric acid being evolved and a greenish liquid formed, which, on the slightest rise of temperature, is converted into a ferric salt. (Berzelius.)—4. The solution of scale-oxide of iron in strong nitric acid yields, after a while, nearly colourless, right-angled four-sided prisms with dihedral summits. These crystals deliquesce in the air, and have a sharp taste. Schönbein regards them as consisting of ferric nitrate, to be immediately described. The solution of the scale-oxide, when heated or exposed to the air, is converted into ferric nitrate, with deposition of yellow flakes. (Vauquelin.)

C. Nitrate of Ferric Oxide, or Ferric Nitrate.—*Pernitrate of Iron.*—Nitric acid, when not too dilute, attacks iron very energetically, great heat being produced, nitric and nitrous oxide evolved, and nitrate of ammonia formed at the same time; if the acid is in excess, a brown solution is formed; if it is deficient, a yellowish-brown basic salt is the result.

a. Acid Salt.—α. Formed by dissolving iron, ferric oxide, or its hydrate in heated nitric acid. The anhydrous oxide dissolves very slowly in nitric acid, much less readily than in hydrochloric acid.—The yellowish-brown solution becomes syrupy on evaporation, and subsequently leaves a brown residue which gives off its acid when gently heated, so that first a basic salt and afterwards pure ferric oxide is left.

β. When 1 volume of the concentrated solution α is mixed with 5 volumes of water, and the yellow mixture gradually heated till it boils, it assumes a deep blood-red colour—retains this colour without becoming turbid, on cooling,—and then, on the addition of a small quantity of nitric acid, deposits the basic salt *b*, β, from which the colourless liquid must be quickly filtered, before the precipitate re-dissolves. The colourless liquid, evaporated to a syrup and then left to itself in close vessels, crystallizes in colourless or pale yellow cubes. The brown solution α,α may also be mixed with an additional quantity of nitric acid: it thereby becomes nearly colourless, and on the subsequent addition of water, loses all its colour, and then, after filtering and evaporation, yields the same cubes. The yellowish colour of the cubes disappears almost wholly when they are dried between bibulous paper, the mother-liquid being thereby absorbed. [Frey (*Kastn. Arch.* 14, 176), by a method which he does not describe, obtained rhombohedrons with truncated edges; angles of the rhombohedron = 78° and 102°.]—The crystals fuse at a temperature below 50°; they deliquesce rapidly in the air, forming a liquid of a honey-yellow colour, and dissolve in all proportions in water. A somewhat concentrated solution turns yellow on each application of heat, the colour being stronger the higher the temperature; a very dilute solution becomes permanently yellow by boiling, and if nitric acid be added to it, after cooling, it again deposits a certain quantity of the basic salt *b*,β. (Schönbein, *Pogg.* 39, 141.)

luble in ammonia, apparently reduced silver.—The composition of ferric azophosphate is as follows :—

Dried at or above 100°.				Gladstone.			
$Fe^{2}O^{3}$	80	34·19		34·48	33·90	34·47	33·62
2P	64	27·35		25·05	25·07		27·93
N	14	5·98		5·67		5·24	
4H	4	1·71				1·94	1·81
9O	72	30·77					
	234	100·00					

Or:

$Fe^{2}O^{3}$	80	34·19
$P^{2}NO^{5}$	118	50·44
4HO	36	15·37
$Fe^{2}O^{3}, P^{2}NO^{5} + 4Aq.$	234	100·00

Dried at 76°.			Gladstone.		
$Fe^{2}O^{3}$	80	32·92	32·33	32·87	
2P	64	26·34	23·92		
N	14	5·76		5·00	
5H	5	2·06		2·36	
10O	80	32·92			
	243	100·00			

Or:

$Fe^{2}O^{3}$	80	32·92
$P^{2}NO^{5}$	118	48·56
5HO	45	18·52
$Fe^{2}O^{3}, P^{2}NO^{5} + 5Aq.$	243	100·00

It is not easy to determine in what state the 5 atoms of water exist in the salt, inasmuch as no appearance of crystallization can be perceived, even with the aid of powerful microscopes; but it is evident that one of the atoms must be differently combined to the rest, since it is driven off at 100°, while the others remain. (Gladstone, *Chem. Soc. Qu. J.* 3, 142.) ¶

D. *Ferrite of Ammonia ?*—Ferric oxide or its hydrate, whether natural or artificial, is always found, after exposure to the air for some time, to contain ammonia.

E. Carbonate of Ferric Oxide and Ammonia.—*Ferrico-ammonic Carbonate.*—When a ferric salt is supersaturated with concentrated carbonate of ammonia, the precipitated ferric hydrate gradually re-dissolves in the liquid. The deep brown-red liquid, if diluted with water, again deposits the hydrated oxide after a while.—Hydrated ferric oxide precipitated by ammonia from a solution of the sesquichloride, and well boiled with potash, is insoluble in carbonate of ammonia, according to Grotthuss; hence the presence of the ammoniacal salt produced in the precipitation, contributes to the re-solution of the hydrate.

F. Phosphate of Ferrous Oxide and Ammonia.—*Ferroso-ammonic Phosphate.*—Formed by mixing a solution of 14 parts of iron in hot hydrochloric acid with a small portion of sulphite of ammonia; adding to it while hot a thoroughly boiled aqueous solution of 100 pts. crystallized ordinary diphosphate of soda, which immediately precipitates white phosphate of ferrous oxide; then adding ammonia in slight excess—immediately closing the flask, which must be completely filled with the liquid—agitating—and leaving the mixture to itself for a few minutes till the precipitate, which is flocculent at first, is converted into laminæ, which sink rapidly to the bottom. If it remains flocculent, the liquid

must be heated again, perhaps with the addition of a small quantity of ammonia; if part only of the precipitate becomes crystalline, the lighter flakes must be separated by levigation from the crystalline laminæ. The laminæ, on which the air no longer exerts any oxidizing action, are then thrown upon a filter, washed with thoroughly boiled water, and dried. No ammonia must be added to the water, because it immediately induces oxidation, so that hydrated ferric oxide remains on the filter, and the water runs off brown; hence also, in preparing the salt, care must be taken not to add too much ammonia.—Greenish-white, soft laminæ, which, when rubbed on the hand, produce a coating like silver; they are permanent in the air; the salt when heated in the air gives off water and ammonia, and leaves, first, greenish ferrous phosphate, amounting to 77 per cent.—then yellowish-white ferric phosphate. With potash-solution it evolves ammonia, and when boiled therewith, gives up its phosphoric acid, and is converted into ferroso-ferric oxide having the form of the original laminæ. Insoluble in water, even at the boiling heat. While yet moist it dissolves readily in acids, even when dilute; but after drying, it dissolves but sparingly and with difficulty, even in concentrated acids. (Otto, *J. pr. Chem.* 2, 409.)

					Otto.
NH^3	17·0	....	9·17	.....	8·77
$2FeO$	70·0	....	37·76	.....	77·00
cPO^5	71·4	....	38·51		
$3HO$	27·0	....	14·56		
$NH^4O, 2FeO, cPO^5 + 2Aq$	185·4	....	100·00		

This composition is analogous to that of phosphate of magnesia and ammonia dried at 100°. (Graham.)

The greenish precipitate which ammonia forms with acid phosphate of ferrous oxide, re-dissolves in excess of ammonia. (A. Vogel.)

G. Phosphate of Ferric Oxide and Ammonia.—*Ferrico-ammonic Phosphate.*—White phosphate of ferric oxide dissolves, with a brown colour, in aqueous ammonia, which may afterwards be expelled by evaporation. (Döbereiner, *Schw.* 26, 271.)

¶ G'. Ammoniacal Azophosphate of Ferric Oxide.—Ferric azophosphate (p. 259) dissolves in ammonia, forming a red solution from which the iron-salt may be again precipitated by the addition of an acid. The ammoniacal solution carefully evaporated over the water-bath, yields a dark red mass very soluble in water, but showing no disposition to crystallize. When treated with water, after being perfectly dried, it separates into two portions, the one soluble containing ammonia, and giving a characteristic precipitate when treated with an acid—the other having the form of micaceous plates of the colour of ferricyanide of potassium: these appear to be chiefly sesquioxide of iron. (Gladstone, *Chem. Soc. Qu. J.* 3, 146.) ¶.

H. Sulphate of Ferrous Oxide and Ammonia.—*Ferroso-ammonic Sulphate.*—To form this salt, a solution of 66 pts. (1 At.) of sulphate of ammonia and 138 pts. (1 At.) of green vitriol is left to crystallize. On mixing equal measures of the saturated solutions of green vitriol and sal-ammoniac, the same salt likewise crystallizes out gradually, while protochloride of iron and ammonium remains in solution. (A. Vogel.) —The crystals $=NH^4O, SO^3 + FeO, SO^3 + 6$ Aq. are isomorphous with

those of sulphate of magnesia and ammonia (III. 248) and many others. *Fig.* 84. (Mitscherlich; *comp.* Marx, *Schw.* 54, 465.) The crystals when purified by re-crystallization, are transparent, and colourless, very hard, and effloresce somewhat above 100°. When heated, they swell up to a white mass, without fusing, and give off water, ammonia, and sulphate of ammonia. Oil of vitriol abstracts their water, and makes them opaque. They are much less soluble in water than green vitriol. (A. Vogel, *J. pr. Chem.* 2, 192.)

I. Sulphate of Ferric Oxide and Ammonia.—*Ferrico-ammonic Sulphate.—a. Basic.*—When a solution of iron in a dilute mixture of sulphuric and nitric acids is exposed to the air, this double salt is precipitated in the form of an ochre, which, when heated, gives off water and ammonia, and afterwards sulphurous acid—is not decomposed by caustic potash—and is but very sparingly soluble in hydrochloric acid. (Berzelius.)

b. Containing Bisulphate of Ferric Oxide.—Formed by adding ammonia to a solution of ammonia-iron-alum till the precipitate begins to be permanent, and leaving the dark brown mixture to evaporate spontaneously.—Transparent, yellowish-brown, short, regular, six-sided prisms, soluble in 2·4 pts. of cold water. (Maus, *Pogg.* 11, 79.)

					Maus.
$2NH^3$	34	....	10·43	.....	10·30
Fe^2O^3	78	....	23·92	.....	23·75
$4SO^3$	160	....	49·08	.....	49·20
$6HO$	54	....	16·57	.....	16·75
$2(NH^4O,SO^3)+Fe^2O^3,2SO^3+4Aq.$	326	....	100·00	.....	100·00

c. Containing Tersulphate of Ferric Oxide.—Crystallizes from a mixture of sulphate of ammonia and tersulphate of ferric oxide in colourless, regular octohedrons and cubo-octohedrons (*Figs.* 2 and 4), the specific gravity of which, according to Kopp, is 1·712. They are soluble in 3 parts of water at 15°. (Forchhammer.) The yellow colour which the salt occasionally exhibits, arises from excess of the iron-salt, and disappears on recrystallization. (Forchhammer; *Ann. Phil.* 5, 406; Berzelius, *Afhandlingar B.* 3; also *Scher. Ann.* 7, 228; Mitscherlich.)

					Forchhammer.
NH^3	17	....	3·54		
Fe^2O^3	78	....	16·25	.....	16·470
Al^2O^3		....		.....	0·260
$4SO^3$	160	....	33·33	.....	34·596
$25HO$	225	....	46·88	.....	43·480
$NH^4O,SO^3+Fe^2O^3,3SO^3+24Aq.$	480	....	100·00		

K. Hydrobromate of Ammonia containing Sesquibromide of Iron.—An aqueous solution of 3 pts. sesquibromide of iron and 2 pts. hydrobromate of ammonia yields, on gentle evaporation, light red needles united in bundles. These crystals, when dissolved and treated with ammonia, yield 2·47 per cent. of ferric oxide. They do not become moist by exposure to the air; are easily soluble in water; and separate from the solution, on evaporation, with a diminished amount of iron, while a mother-liquid richer in iron remains. (Löwig.)

L. Ammonio-protochloride of Iron.—Protochloride of iron absorbs ammoniacal gas with avidity, and swells up to a white powder which

gives up its ammonia when heated, but on the addition of water, is partly resolved into hydrochlorate of ammonia and hydrated ferrous oxide. (Faraday.)

M. PROTOCHLORIDE OF IRON AND AMMONIUM. — *Ferroso-ammonic Chloride.*—By boiling iron filings with a saturated solution of sal-ammoniac in a close vessel—whereupon hydrogen and ammoniacal gas are evolved—and leaving the solution to crystallize by cooling. (Hisinger & Berzelius, *Gilb.* 27, 273.)—2. By mixing saturated solutions of green vitriol and sal-ammoniac in equal volumes—allowing the ferroso-ammonic sulphate to crystallize out—pouring off the remaining liquid and evaporating it to the crystallizing point—and separating the crystals mechanically from the sal-ammoniac which crystallizes out with them. (A. Vogel, *J. pr. Chem.* 2, 192.)—3. An aqueous solution of 1 pt. protochloride of iron and 4 pts. sal-ammoniac, prepared hot and filtered, is set aside for 24 hours in a closed vessel—and the resulting crystals dried as quickly as possible, and kept in stoppered bottles. (Winckler, *Repert.* 59, 171.)—Prepared by (1): bluish-green crystals, which, when exposed to the air, become covered with hydrated ferric oxide, and whose aqueous solution is not precipitated by ammonia, unless the air has access to it. (Hisinger & Berzelius.)—By (2): lemon-yellow, transparent octohedrons which neither deliquesce nor effloresce in the air—give off sal-ammoniac when heated—and are easily soluble in water, but not in alcohol. (A. Vogel.)—By (3): transparent and colourless rhombohedrons, which have a sharp saline and afterwards astringent taste, contain 11·2 per cent. of ferrous chloride, turn yellowish in the air, and are easily soluble in water. (Winckler.)

N. AMMONIO-SESQUICHLORIDE OF IRON. — Sesquichloride of iron slowly absorbs ammoniacal gas at ordinary temperatures, producing a slight disengagement of heat, but without alteration of external appearance. Part of the compound volatilizes undecomposed when heated; the rest leaves protochloride of iron. It deliquesces in the air, but less quickly than pure sesquichloride of iron. When thrown into water in considerable quantities, it dissolves with a hissing noise; the solution is dark red and transparent. (H. Rose, *Pogg.* 24, 302.)

					H. Rose.
NH^3	17·0	....	9·59	.....	9
Fe^2Cl^3	160·2	....	90·41	.....	91
NH^3, Fe^2Cl^3	177·2	....	100·00	.....	100

O. SESQUICHLORIDE OF IRON AND AMMONIUM.—*Ferrico-ammonic Chloride.*—1. A solution of sal-ammoniac in a large excess of ferric hydrochlorate, when evaporated over oil of vitriol within a receiver containing air, yields garnet-coloured crystals belonging to the oblique prismatic system, which may easily be mistaken for regular octohedrons; they are not decomposed by water like the corresponding compound of chloride of potassium. (Fritzsche, *J. pr. Chem.* 18, 484.)—2. By slowly evaporating a mixture of this nature, the author obtained very deliquescent rectangular octohedrons, having two of the basic edges and four of the basic angles truncated.

					Fritzsche.
$2NH^4$	36	....	12·63		
$2Fe$	54	....	18·95	.....	19·47
$5Cl$	177	....	62·10	.....	61·66
$2HO$	18	....	6·32		
$2NH^4Cl + Fe^2Cl^3 + 2Aq.$	285	....	100·00		

Or:			
$2NH^3,HCl$	106·8	.....	37·47
Fe^2Cl^3	160·2	.....	56·21
$2HO$	18·0	.....	6·32
$2(NH^3,HCl),Fe^2Cl^3+2Aq.$	285·0	.....	100·00

P. Sal-ammoniac containing Sesquichloride of Iron.—A solution of from 3 to 24 parts of sal-ammoniac and 1 part of sesquichloride of iron in water yields on evaporation, aurora-red transparent crystals. According to Geiger, these crystals are acute rhombohedrons when they contain a medium quantity of iron, but obtuse when the proportion of iron is either very small or very large; according to Marx also (*Schw.* 54, 304), they appear to be made up of a great number of small cubes not quite regularly grouped together, whereby the cubical shape is somewhat altered. (Gm.)—The quantity of iron is small and variable. If 24 parts of sal-ammoniac are used to 1 part of the ferric chloride, the crystals contain 0·85 per cent. of ferric chloride; if 14 parts of sal-ammoniac are used, they contain 1·93; and with 3 sal-ammoniac, they contain 5·12 per cent. of ferric chloride. The mother-liquor of the last-mentioned crystals yields, on further evaporation, brown-red crystalline granules, containing 5·75 per cent. of ferric chloride. (Geiger.) When 10 pts. sal-ammoniac have been used with 1 pt. ferric chloride, the crystals contain 0·86 per cent. of the latter. (Winckler, *Repert.* 67, 155.) The crystals, when heated, become yellow and opaque, and evolve, first sal-ammoniac, and afterwards ferric chloride. They dissolve in 3 parts of cold water; those in which the proportion of ferric chloride does not exceed 5·12 per cent., become moist only in damp air; those which contain 5·75 p. c. Fe^2Cl^3, become moist even in dry air. (Geiger, *Repert.* 13, 422.) When their aqueous solution is evaporated, sal-ammoniac crystallizes out, nearly pure at first, but afterwards continually richer in iron, being first yellow and then red, and there remains a mother-liquid richer in iron.

To these mixtures of ferric chloride and sal-ammoniac, belong the *Ferruginous Flowers of Sal-ammoniac, Flores Salis-ammoniaci martiales.* These are obtained:—1. By subliming 16 pts. sal-ammoniac with 1 pt. ferric oxide, whereupon ammonia is evolved; or with 1 pt. iron filings, in which case hydrogen is set free and protochloride of iron and ammonium is produced, the latter, however, if the air has moderately free access to it, is converted into sesquichloride of iron and ammonium, while ferric oxide is left behind.—2. By subliming a mixture (obtained by evaporation) of 12 parts sal-ammoniac and hydrochlorate of ferric oxide prepared from 1 part of iron filings.—3. By dissolving 16 pts. sal-ammoniac and 1 pt. ferric chloride in water and evaporating to dryness. Some pharmacopœias, however, direct the preparation of the crystals above described. Yellow saline mass, which is yellower and more deliquescent in proportion as it is richer in iron.

Iron and Potassium.

A. Alloy of Iron and Potassium.—Formed in the preparation of potassium by method No. 2 (III. 5), when pieces of iron happen to be situated at the lower end of the gun-barrel where it projects from the furnace.—Whiter than iron, malleable, and so soft that it will often take

impressions from the nails; more fusible than iron. Oxidizes in the air; effervesces with water and with aqueous acids. (Gay-Lussac & Thénard.)

B. FERRITE OF POTASH.—1. When hydrate of potash is fused in an iron crucible, and the whole digested in water after cooling, a portion of ferric oxide (ferrous acid) is dissolved together with the potash.—2. When recently precipitated hydrate of ferric oxide is boiled for an hour with strong caustic potash, a very pale yellow liquid is obtained containing a small portion of ferric oxide. (Chodnew, *J. pr. Chem.* 28, 221.)

C. FERRATE OF POTASH.—Becquerel (*Ann. Chim. Phys.* 51, 105) found that ferric oxide ignited in a silver crucible with from 4 to 6 times its weight of potash-hydrate, dissolved in the potash, but was separated again, with evolution of oxygen, when the potash was dissolved in water; this escape of oxygen was attributed by Becquerel to the presence, not of ferric acid but of peroxide of potassium.—Ferrate of potash is formed when iron or ferric oxide is heated to redness with nitre or peroxide of potassium, or—if air has access to the mixture—with hydrate of potash. It is also produced by the action of chlorine on ferric oxide diffused through a strong solution of potash (Fremy, *J. Pharm.* 27, 97; also *J. pr. Chem.* 26, 108); and by galvanic action. ¶ The existence of ferric acid appears to have been known to Stahl, who observed that when iron is calcined with nitre and the mass digested in water, the caustic alkali produced by the calcination of the nitre takes up part of the iron, forming an amethyst or purple solution; also, that if a very dilute solution of iron in nitric acid be poured by small portions at a time into very strong caustic potash and the liquid agitated, the iron dissolves and imparts a blood-red colour to the liquid.—Subsequently, Eckeberg (*Kongl. Vetensk. Handl.* 1802, p. 68; also *Scher. J.* 9, 607) on fusing gadolinite with caustic potash, obtained an alkaline solution which had a dark red colour and deposited a brick-red compound of iron and lime. And in a note he adds that the red colour is not due to manganese, for even iron alone can dissolve in caustic potash and produce the most beautiful purple colour, provided it has been previously roasted. (*J. pr. Chem.* 32, 448; *comp.* Kopp, *Geschichte d. Chem.* 1, 192.) ¶

Preparation of the dry salt.—1. By igniting ferric oxide very strongly for some minutes with nitre and hydrate of potash. If the heat is too low, nitrite of potash remains undecomposed, and then, on the addition of water, reduces the ferric acid to the state of sesquioxide. (Fremy.)—A mixture of 1 part of finely pulverized ferric oxide and 4 parts of nitre is introduced into a crucible capable of containing double the quantity; the cover luted on tight, but in such a manner as to leave an exit for the gas; and the mixture heated—for an hour if the quantity is 6 ounces, for a shorter time if it be smaller—to a bright red heat, but not higher. (Denham Smith, *Phil. Mag. J.* 23, 217.)—2. By igniting iron-filings with nitre. (Fremy.)—An intimate mixture of 1 pt. finely divided iron and 2 pts. dry nitre is introduced into a capacious crucible kept at a dull red heat, and the crucible removed from the furnace as soon as the mixture begins to deflagrate and form a white cloud, an effect which begins at one point and quickly extends throughout the whole mass. If the temperature is too high, the compound is decomposed as soon as formed. (H. Trommsdorff, *N. Br. Arch.* 29, 104.) If the crucible is too hot, the nitre fuses without deflagrating. The mass must then be poured

into an iron mortar and again introduced into the crucible after cooling. The crucible should therefore be heated so as to exhibit perceptible redness only at the bottom and a few inches above, and the mixture should be thrown into the middle and somewhat to the side: the deflagration—which is unattended with danger—then takes place in a few seconds with a bright glow and intumescence of the mass. The crucible is removed from the fire either during or immediately after the deflagration, and the soft, somewhat friable mass taken out with an iron spoon. As, however, ferrate of potash thus obtained is contaminated with nitrite, the red solution which it forms in water quickly loses its colour. (Wackenroder, *N. Br. Arch.* 33. 41.—3. By igniting ferric oxide for a considerable time with hydrate of potash. Fremy.)—The red-brown or reddish, highly deliquescent mass thus obtained is quickly pulverized, and preserved in dry, well-stopped bottles.

Aqueous Ferrate of Potash—1. Formed by dissolving the dry salt in cold water. Since the act of solution is attended with evolution of heat, by which a portion of the salt is decomposed, it is necessary to use ice-cold water: there is always, however, a slight evolution of oxygen gas, probably arising from peroxide of potassium. The solution must be separated from the undissolved portion by subsidence and decantation, not by filtering. (D. Smith.)—2. By passing chlorine gas through a very strong solution of potash in which ferric oxide is diffused, till the oxide dissolves and forms a red solution. (Fremy.) When 5 parts of hydrated ferric oxide, recently precipitated and dried between bibulous paper, 10 parts of hydrate of potash, and 16 of water are used, and chlorine rapidly passed through the solution, the oxide quickly dissolves in the liquid, which gradually rises in temperature, and deposits chlorate of potash on cooling; if too much water or too much ferric hydrate is used, the liquid remains colourless. (Wackenroder.) The chlorine must not be in excess, otherwise it will decompose the salt. (H. Rose.)—3. Poggendorff's process consists in passing the positive electricity of a six-pair Grove's battery (I. 422) for 24 hours, through an electrode of English cast-iron, into a solution of caustic potash concentrated as much as possible and surrounded with ice; in that solution there is likewise immersed a clay cylinder filled with caustic potash, and the negative electricity is conducted into the latter liquid by means of a platinum plate. If a more dilute solution of potash is used, the resulting preparation is less permanent. No oxygen gas is evolved on the iron plate, excepting just at the beginning of the action or a little after; if the current be long continued, microscopical crystals of ferrate of potash are deposited on this plate; a small quantity of iron collects on the platinum plate. (H. Rose, *Pogg.* 59, 315.)

Aqueous ferrate of potash is of a deep amethyst-red or cherry-red colour, and pervious to light only when in very thin strata.—The solution when left to stand for some time, loses its colour, gives off oxygen gas, and yields a precipitate of hydrated ferric oxide, the decomposition taking place the more quickly as the solution is warmer and more dilute. (Fremy.) The concentrated solution obtained by (2), if kept in close vessels, does not decompose completely, even in the course of several months, but leaves a red residue when evaporated. (D. Smith.) At 100°, the decolorization is instantaneous. (Fremy.) The concentrated solution obtained by (3) sustains a boiling heat without decomposition, but afterwards deposits ferric oxide more quickly than if it had not been boiled; it

is altogether more permanent than that obtained by (2), retains its deep red-colour for months, and deposits but little ferric oxide all the while. Dilution with various potash and soda-salts produces less tendency to decomposition than dilution with pure water. When the solution, after long standing, has deposited all its ferric oxide, it exhibits a green colour, arising from manganate of potash formed from manganese contained in the cast-iron. (H. Rose.)—Sulphuric or nitric acid forms a double salt of ferric oxide and potash, with liberation of oxygen gas (Fremy); hydrochloric acid likewise forms a double salt, with evolution of chlorine (D. Smith); a smaller quantity of acid causes a precipitation of ferric oxide (Fremy). With zinc-salts the solution evolves oxygen; from manganese and nickel-salts it precipitates the peroxides. (Smith.) Other heavy metallic salts and alum likewise decolorize the liquid, the base being precipitated together with ferric oxide. (Wackenroder.)—The compound is quickly decomposed by de-oxidizing agents. Sulphurous acid forms sulphate of potash and precipitates ferric oxide. (H. Rose.) Sulphuretted hydrogen colours the solution (2) dark green by forming sulphide of iron (Wackenroder); the concentrated solution (3) is converted by the same reagent into a black mass, which forms a deep green liquid with a large quantity of water. (H. Rose.)—Ammonia and all ammoniacal salts decompose the compound, because the ammonia which is evolved reduces the ferric acid to ferric oxide. (Wackenroder, H. Rose.)—All organic substances act in the same manner; hence the solution cannot be filtered through paper. (Fremy.) Oxalic acid mixed with the solution gives off carbonic acid and oxygen gas. (D. Smith.) Alkaline racemates, tartrates, and malates quickly decolorize the liquid, without precipitating ferric oxide; alkaline citrates act very slowly and occasion a precipitation of ferric oxide. Oxalate, acetate, formiate, and benzoate of potash decolorize the liquid as slowly as the inorganic salts of potash; and succinate of potash acts still more slowly. Alcohol (with formation of aldehyde, apparently) sugar, and white of egg, decolorize it quickly, the former with, the latter without, precipitation of ferric oxide. (H. Rose.) Ferrocyanide of potassium likewise exerts a decolorizing action. (Wackenroder.)

The solution (1) if boiled till completely decolorized evolves 25·67 pts. oxygen gas for every 100 pts. of precipitated ferric oxide. [This is equivalent to 10·01 pts. (not quite $1\frac{1}{2}$ At.) oxygen to 39 pts. ($\frac{1}{2}$ At.) ferric oxide.] Since the liquid can only be separated from the undissolved oxide by decantation, it is possible that some portion of the oxide still remained suspended in it, in which case, the proportion of oxygen to the ferric oxide would come out too small. On the supposition that ferric acid is FeO^3, 12 pts. of oxygen should be evolved for every 39 pts. of ferric oxide. (D. Smith.)—By passing sulphurous acid gas through the solution (3) till the colour is destroyed, and determining the quantity of ferric oxide precipitated and sulphuric acid produced (by supersaturating the filtrate with hydrochloric acid and precipitating with chloride of barium) 349·8 pts. (3 At.) of sulphate of baryta were found to correspond, in different experiments, to the following quantities of ferric oxide: 73·1; 78·3; 81·9; therefore approximately 78 pts. (1 At.) Hence ferric acid= FeO^3; and when it is decomposed by sulphurous acid, 3 At. sulphuric acid are produced for each atom of ferric oxide. (H. Rose.)

$$2FeO^3 + 3SO^2 = Fe^2O^3 + 3SO^3.$$

When 1 pt. ferric oxide is ignited as above (p. 265) with only 2 pts. nitrate

of potash (or better with nitrate of soda), and the mass digested in water, a beautiful green solution is obtained like that of mineral chameleon, and always mixed with the red salt: the latter, however, is soon decomposed, whereas the green salt may be kept in close vessels for a longer time. This green salt appears to contain an acid with a smaller quantity of oxygen. Chlorine colours the solution red; acids likewise redden the liquid, with evolution of oxygen, and afterwards decolorize it. The green liquid may be passed through paper without decomposition, but it is decomposed by prolonged contact with organic substances. (D. Smith.)

D. Carbonate of Ferric Oxide and Potash.—*a. Ferrico-potassic Carbonate.—Stahl's Alkaline Tincture of Iron.*—When a ferric salt is supersaturated with strong carbonate of potash, the precipitated ferric hydrate is re-dissolved and forms a blood-red solution. This solution is decomposed, with precipitation of ferric hydrate, both by heat, and by dilution with water or with caustic potash. (Hausmann, *Scher. J.* 4, 576; Proust, *N. Gehl.* 3, 560; Döbereiner, *Schw.* 9, 1.) Freshly precipitated ferric hydrate is not soluble in strong carbonate of potash, so that the presence of the potash-salt formed at the same time appears to be necessary to the solution. (Grotthuss, *Schw.* 30, 71.)

E. Boride of Iron and Potassium.—The three substances combine at a white heat, and form a blackish mass which exhibits the metallic lustre, conducts electricity, effervesces slightly in water, and when treated with hydrochloric acid, yields ferrous oxide and boracic acid. (H. Davy.)

F. Sulphide of Iron and Potassium.—*a.* When sulphide of antimony is ignited with iron, carbonate of potash, and charcoal, an easily fusible slag is obtained. (Berthier.)

b. Iron filings placed in contact with solution of potassic liver of sulphur, turn black and impart a green colour to the liquid. (Vauquelin.)

c. The concentrated solution of ferrate of potash obtained by (3) is converted by sulphuretted hydrogen into a black mass probably consisting of KS,FeS^3; this forms a dark green liquid with water, which remains green even when very much diluted. The solution remains permanent in the air for a long time. Continued boiling decomposes the concentrated solution, with separation of sulphide of iron; the dilute solution undergoes no alteration, excepting that it acquires a transient brown tint every time it is heated. (H. Rose, *Pogg.* 59, 320.)

G. Sulphate of Ferrous Oxide and Potash.—*Ferroso-potassic Sulphate.*—$KO,SO^3 + FeO,SO^3 + 6$ Aq.—Formed by dissolving iron-filings in a warm aqueous solution of bisulphate of potash. Greenish crystals, which have the form of sulphate of magnesia and ammonia, refract light doubly, have a rough taste, and fall to pieces when exposed to the air. (Link, *Crell. Ann.* 1796, 1, 30; Mitscherlich; Brewster, *Schw.* 33, 344.)

H. Sulphate of Ferric Oxide and Potash. — *Ferrico-potassic Sulphate.* — *a. Yellow Iron-ore.* Ochre-yellow, homogeneous, massive plates; sp. gr. 2·78...2·9; fracture varying from flatly conchoidal to earthy. When heated, it turns red, evolves water and afterwards sulphurous acid; gives up nothing to boiling water; slightly soluble in hydrochloric acid, more readily in aqua-regia. (Rammelsberg, *Pogg.* 43, 134.)

	Yellow Iron-ore, from Kolostruk.		Rammelsberg.
KO	47·2	7·37	7·88
CaO			0·64
$4Fe^2O^3$	312·0	48·73	46·74
$5SO^3$	200·0	31·25	32·11
9HO	81·0	12·65	13·56
$KO,SO^3 + 4(Fe^2O^3,SO^3) + 9Aq.$	640·2	100·00	100·93

b. Remains in the form of a pale yellow powder when the salt *c* is treated with hot water. (Anthon.)

			Anthon.
KO,SO^3	87·2	8·09	8·0
$6Fe^2O^3$	468·0	43·45	41·4
$9SO^3$	360·0	33·42	35·6
18HO	162·0	15·04	15·0
$KO,SO^3 + 3(2Fe^2O^3,3SO^3) + 18Aq.$	1077·2	100·00	100·0

c. Formed by adding potash to a solution of potash-iron-alum till a permanent precipitate begins to form—or rather by adding a smaller quantity of potash, so that a considerable quantity of iron-alum may remain undecomposed—and leaving the dark liquid to evaporate freely in a shallow dish.—Yellowish-brown, transparent, regular six-sided prisms, shortened into tables; when heated, they give off their water of crystallization, but retain their form. Their solution in cold water, 6 parts of which are required to dissolve them, is soon decomposed—unless it likewise contains potash-iron-alum—into precipitated disulphate of ferric oxide, and iron-alum which remains in solution. (Maus, *Pogg.* 11, 78.)—The same salt has been accidentally obtained in the preparation of iron-alum: 1. A solution of 78 pts. ferric oxide, 147 oil of vitriol, and 87·2 sulphate of potash, deposited—partly during concentration—dark brown crystalline crusts, which gave off water and assumed a red-brown colour at a temperature below redness, and evolved sulphuric acid at a white heat, leaving a residue of ferric oxide mixed with sulphate of potash. The salt dissolves in 12·75 parts of water at 10°; but, when heated with water, it is resolved into salt *b*, and a red-brown solution, which deposits, on evaporation, first the salt *c* and then iron-alum. (Anthon, *Repert.* 76, 361.)—2. If a boiling solution of sulphate of potash be added to an over-concentrated solution of ferric sulphate, a small, greenish-yellow, crystalline precipitate is produced, having the composition given below; after several days' standing, however, it disappears again, with formation of iron-alum. Also, when crystallized iron-alum is dissolved in a small quantity of hot water, the greenish-yellow salt is deposited first. (W. Richter, *N. Br. Arch.* 23, 316.)

			Maus.	Anthon.	Richter.
2KO	94·4	24·43	23·1	20·5	22·2
Fe^2O^3	78·0	20·19	20·8	21·2	21·5
$4SO^3$	160·0	41·41	41·7	42·6	42·1
6HO	54·0	13·97	14·4	15·4	14·2
$2(KO,SO^3) + Fe^2O^3,2SO^3 + 6Aq.$	386·4	100·00	100·0	99·7	100·0

d. When carbonate of potash is added, with agitation, to an aqueous solution of tersulphate of potash, as long as no permanent precipitate is formed, and the dark brown liquid (which becomes turbid when filtered as well as when heated) is mixed with a large excess of alcohol, a light reddish-yellow precipitate is formed, which must be washed with alcohol.

This precipitate, while yet moist, is soluble in water, but after it is dry, water decomposes it, leaving basic sulphate of ferric oxide undissolved. The aqueous solution deposits a light yellow ochre on standing, and more quickly on boiling, losing at the same time the greater part of its colour. (Soubeiran, *Ann. Chim. Phys.* 44, 329.)

					Soubeiran.
2KO	94·4	...	11·15	.....	11·4
$3Fe^2O^3$	234·0	...	27·64	.....	26·6
$8SO^3$	320·0	...	37·81	.....	37·0
22HO	198·0	...	23·40	.....	24·0
$2(KO,SO^3)+3(Fe^2O^3,2SO^3)+22Aq.$	846·4	...	100·00	.....	99·0

e. Potash-iron-alum.—78 parts of ferric oxide are dissolved in 147·2 pts. oil of vitriol mixed with water and heated, and 87·2 pts. sulphate of potash added thereto, or 276 pts. (2 At.) green vitriol mixed with 49 pts. oil of vitriol, are oxidized by nitric acid at a boiling heat, and 87·2 pts. sulphate of potash added to the liquid; or, according to Heintz's method, 10 parts of pounded crystals of green vitriol are heated with 4 parts of nitre and 5 of sulphuric acid, till no more nitrous acid is evolved,—then dissolved in a fourfold quantity of water at 80°, and filtered. When the concentrated solution is left to stand for some time at a temperature of 0°, or somewhat above, the alum crystallizes out; and by taking out the crystals first obtained, and putting them in again after evaporating the liquid a little further, very large crystals may be obtained. The mother-liquid, mixed with a small quantity of sulphuric acid and evaporated, deposits a white granular powder or crystalline crust, consisting of iron-alum with only 8·5 or 9 per cent. (3 At.) water of crystallization; this, when quickly washed with cold water and then dissolved in warm water, yields more octohedrons. If the remaining mother-liquid be still further evaporated till nothing remains but a saline mass mixed with fluid, and this mass quickly washed, iron-alum is left, containing only 2·9 to 3·3 p.c. (1 At.) water. Commercial iron-alum contains a large quantity of alumina. (W. Heintz, *Pogg.* 55, 331.)

Regular octohedrons. Pale violet. (Richter, Heintz, Gmelin.) Colourless, according to other authorities.

Iron-alum, when exposed to the air, becomes slowly covered with a white powder. (W. Richter.) It fuses in its water of crystallization, afterwards gives off its water, and is converted into a yellowish-white, spongy mass resembling burnt alum. When very strongly ignited, it fuses, gives off 24·4 per cent. of sulphuric acid, and leaves a mixture of 15·1 per cent. ferric oxide and 17 p. c. sulphate of potash. (W. Richter, *Report.* 76, 361.) Iron-alum is resolved by heat into the salt *c*, tersulphate of ferric oxide, and free sulphuric acid.

$$2(KO,SO^3+Fe^2O^3,3SO^3) = [2(KO,SO^3)+Fe^2O^3,2SO^3]+Fe^2O^3,3SO^3+SO^3.$$

When, therefore, pulverized iron-alum is dried over oil of vitriol between 60 and 100°, it first becomes moist and then leaves a brownish-yellow powder, which, if treated with water, will perhaps yield a few more octohedrons; but these are probably reproduced alum. (Heintz.) When iron-alum is dissolved in a small quantity of hot water, the greenish-yellow salt *c* is likewise deposited at first, but it is afterwards reconverted into alum and redissolved. (Richter.) Iron-alum dissolves in 5 parts of water at 12·5°. (Anthon.)

	Crystallized.			Anthon.	Richter.
KO	47·2	...	9·42	9·2	10·3
Fe^2O^3	78·0	...	15·56	15·1	14·9
$4SO^3$	160·0	...	31·92	32·2	30·9
24HO	216·0	...	43·10	43·5	43·5
$KO,SO^3+Fe^2O^3,3SO^3+24Aq.$	501·2	...	100·00	100·0	99·6

I. Protochloride of Iron and Potassium. — *Ferroso-potassic Chloride.*—When the concentrated solutions of the two metallic chlorides are mixed and the mixture cooled or gently evaporated, bluish-green, hydrated crystals are obtained. (Berzelius.)

K. Sesquifluoride of Iron and Potassium.—*Ferrico-potassic Chloride.*—A solution of chloride of potassium in excess of ferric hydrochlorate evaporated under a bell-jar over oil of vitriol, yields small yellowish-red crystals belonging to the oblique prismatic system. A small quantity of water extracts chloride of iron from them and leaves crystals of chloride of potassium undissolved, as may be seen by examination with the microscope. A larger quantity of water dissolves the whole; but on evaporation, colourless crystals of chloride of potassium separate out first, and afterwards coloured crystals of the ferrico-potassic chloride; and at this degree of concentration, the crystals of chloride of potassium re-dissolve without any warming or stirring, and are re-converted into crystals of ferrico-potassic chloride. (Fritzsche, *J. pr. Chem.* 18, 483.)

	Crystallized.			Fritzsche.
2KCl	149·2	....	45·57	44·72
2Fe	54·0	....	16·49	17·17
3Cl	106·2	....	32·44	31·39
2HO	18·0	....	5·50	
$2KCl,Fe^2Cl^3+2Aq.$	327·4	....	100·00	

L. Protofluoride of Iron and Potassium. — *Ferroso-potassic Fluoride.*—KF,FeF.—Precipitated on mixing hydrofluate of potash with sulphate of ferrous oxide. (Berzelius.)

M. Sesquifloride of Iron and Potassium. — *Ferrico-potassic Fluoride.*—*a. Terbasic.*—Formed by dropping aqueous sesquifluoride of iron into excess of fluoride of potassium.—*b. Bibasic.*—By the contrary process.—In both cases, small colourless crystals are obtained somewhat soluble in water, especially in hot water. (Berzelius, *Pogg.* 4, 129.)

	a. $3KF,Fe^2F^3$.				*b.* $2KF,Fe^2F^3$.			Berzelius.
3K	117·6	....	41·44	2K	78·4	....	34·71	33·88
2Fe	54·0	....	19·03	2Fe	54·0	....	23·90	24·06
6F	112·2	....	39·53	5F	93·5	....	41·39	
	283·8	....	100·00		225·9	....	100·00	

Iron and Sodium.

A. Ferrite of Soda.—78 pts. (1 At.) of ferric oxide mixed with excess of ignited carbonate of soda, drive off, at a red-heat, 23·19 (a little more than 1 At.) carbonic acid, and form a difficultly fusible mixture. This mixture, when cool, is liver-coloured—has a waxy, conchoidal

fracture—and takes up carbonic acid from the air, becoming red-brown and dull. Water either hot or cold dissolves out the caustic soda (together with the excess of carbonate), and leaves ferric oxide free from soda: the latter is brown-black after drying, and dissolves easily in dilute hydrochloric acid, but a small quantity of magnetic oxide (about 2·1 per cent. of the ferric oxide) usually remains undissolved. (Count Schaffgotsch, *Pogg.* 43, 117.)

B. Carbonate of Ferric Oxide and Soda.—Analogous to carbonate of ferric oxide and potash.

C. and D.—With *Borax*, ferric oxide yields upon charcoal in the inner flame, a dark bottle-green glass, which, by more complete reduction to the state of ferrous oxide, acquires a lighter bluish-green colour, and, if the quantity of iron is but small, appears colourless after cooling. The reduction is accelerated by addition of tin. In the outer flame, a yellowish-red glass is produced, which on cooling becomes yellow and afterwards colourless, if the quantity of ferric oxide is but small, but remains yellow if it be larger.—*Microcosmic Salt* behaves like borax. (Berzelius.)

¶ E. Pyrophosphate of Ferrous Oxide and Soda.—*Ferroso-sodic Pyrophosphate.*—Exists only in solution, and when exposed to the air, turns red and yields a deposit. Sulphuretted hydrogen colours it brown, and sulphide of ammonium precipitates it completely. (Persoz, *Ann. Pharm.* 65, 170.)

F. Pyrophosphate of Ferric Oxide and Soda.—*Ferrico-sodic Pyrophosphate.*—Obtained by boiling pyrophosphate of ferric oxide with a quantity of pyrophosphate of soda not sufficient to dissolve it, and precipitating with alcohol. (Fleitmann & Henneberg, *Ann. Pharm.* 65, 390.)—Colourless and easily soluble. The solution may be evaporated to a syrupy consistence without becoming turbid; but is partially decomposed thereby, like the alumina-salt. No turbidity or colour shows itself even after the solution has been left to evaporate spontaneously for a month. When treated with sulphuretted hydrogen, it assumes the colour of catechu, without yielding a deposit of sulphur; and on the addition of sulphide of ammonium, a deep green colour is produced. A precipitate likewise appears after a while, but it re-dissolves on being washed and yields a greenish-brown solution. The formula of this salt is $P^{1\frac{1}{2}}O^{7\frac{1}{2}},Fe^2O^3+(PO^5,2NaO)+x\,Aq.$ (Persoz), or $2Fe^2O^3,3PO^5+2(2NaO,PO^5)+7\,Aq.$ (Fleitmann & Henneberg.) ¶

					Fleitmann & Henneberg.
$2Fe^2O^3$	156	....	22·29	....	22·42
$4NaO$	124	....	17·71		
$5PO^5$	357	....	51·00	....	51·12
$7HO$	63	....	9·00	....	9·19
$2Fe^2O^3,3PO^5+2(2NaO,PO^5)+7Aq.$	700	....	100·00		

G. Sulphide of Iron and Sodium.—1. Formed by fusing 2 parts of iron pyrites with 1 pt. carbonate of soda.—2. By fusing sulphide of antimony with carbonate of soda, charcoal, and iron.—Deep yellow, forms a black paste with water. (Berthier.)

Iron and Calcium.

Aqueous ferrate of potash does not precipitate the salts of strontia, lime, or magnesia. (D. Smith.)

A. Hypophosphite of Ferric Oxide and Lime.—An aqueous solution of phosphite of lime is boiled for a considerable time with excess of ferrous oxalate, the mixture left to cool in a closed vessel, then quickly filtered and evaporated in vacuo over oil of vitriol.—Greenish crystalline crusts, which, when heated, give off spontaneously inflammable phosphuretted hydrogen gas. Contains 31·37 hypophosphite of lime, 44·73 hypophosphite of ferrous oxide, and 23·90 water. (H. Rose, *Pogg.* 12, 294.)

B. Sulphide of Iron and Calcium.—When 20 pts. crystallized gypsum and 20 dry ferrous sulphate are heated to whiteness in a charcoal crucible, 17·23 parts of metallic sulphide are obtained, in the form of a fused, blistered, whitish-grey mass, having a faint metallic lustre. (Berthier.)

Fluorspar fuses readily with ferric sulphate; but the mixture decomposes immediately afterwards, with evolution of sulphuric acid. (Berthier, *Ann. Chim. Phys.* 43, 301.)

Iron and Magnesium.

A. Alloy of Iron and Magnesium.—Magnesia moistened with oil and brought to the melting point before the oxy-hydrogen blowpipe, fuses with iron into a brittle alloy, which exhibits the metallic lustre, and yields to the file. (Clarke.)

B. Carbonate of Ferrous Oxide and Magnesia.—*Mesitine-spar*, which has the form of calcspar and a density of 3·36, is, according to Stromeyer, $MgO,CO^2 + FeO,CO^2$.

Carbonate of magnesia appears to render hydrated ferric oxide somewhat soluble in water. (Bischof, *J. pr. Chem.* 2, 70.)

C. Sulphate of Ferroso-ferric Oxide and Magnesia.—*Botryogene.*—Hyacinth-red, oblique rhombic prisms; sp. gr. 2.039. Contains from 2·22 to 6·71 p. c. sulphate of lime, 26·88 to 17·10 sulphate of magnesia, 35·88 to 39·92 ferroso-ferric sulphate, 6·77 to 6·85 basic ferric sulphate, and 28·28 to 31·42 water, including loss. (Berzelius & Haidinger, *Pogg.* 12, 491.)

Iron and Cerium.

Carbide of Iron and Cerium.—A mixture of ceric and ferric oxides heated to whiteness with charcoal, yields a green, porous, magnetic, very brittle mass, which appears metallic when filed. (Gahn.)

Iron and Glucinum.

A. Alloy of Iron and Glucinum.—Obtained by Sir H. Davy: 1. By heating to whiteness a mixture of glucina, iron, and potassium;

2. By bringing slightly moistened glucina inclosed in an atmosphere of hydrogen into the circuit of a thousand-pair voltaic battery with double plates, the negative pole being formed of an iron wire, which was fused by the action of the current.

B. Carbide of Iron and Glucinum.—By raising a mixture of glucina, iron, and lamp-black to an intense white heat.—Whiter and less ductile than iron. Dissolves in acids, forming double salts of iron and glucinum. (Stromeyer.)

Iron and Aluminum.

A. Alloy of Iron and Aluminum.—Prepared by Davy in the same, manner as the alloy of iron and glucinum (method 2).—Whiter than iron. When immersed in water, it causes effervescence, and becomes covered with a white powder. Dissolves in hydrochloric acid, forming a mixture of hydrochlorate of ferrous oxide and hydrochlorate of alumina.

B. Aluminate of Ferrous Oxide.—*Zeilanite.*—Spinelle (III., 328) in which part of the magnesia is replaced by ferrous oxide.—Black octohedrons (*Figs.* 2 and 6). Sp. gr. from 3·6 to 3·8. Harder than quartz; translucent or opaque; yields a greyish-green powder. Does not fuse before the blowpipe, but dissolves in borax or in microcosmic salt, forming a glass coloured by iron, and scarcely acted upon by acids.

	At.	*Zeilanite.*		Abich. Ural.	Abich. Iserwiese.	At.		Abich. Vesuvius.
MgO	2	40·0	17·45	17·58	17·70	9	180	24·69	25·94
FeO	1	35·0	15·27	13·97	19·29	1	35	4·80	5·06
Al^2O^3	3	154·2	67·28	65·27	59·66	10	514	70·51	67·46
SiO^2				2·50	1·79				2·38
		229·2	100·00	99·32	98·44		729	100·00	100·84

Addendum.—*Chlorospinelle,* from Slatoust.—Regular octohedrons; sp. gr. 3·593; hardness equal to that of topaz. Translucent at the edges, grass-green, yielding a greyish-green powder; assumes a transient brownish-green colour when heated. Infusible before the blowpipe; fuses with carbonate of soda to a greyish-white mass; in the state of powder, it dissolves readily in borax or in microcosmic salt, forming a green glass, colourless after cooling. It may be regarded as spinelle, MgO,Al^2O^3, in which part of the alumina is replaced by ferric oxide, as is the case, though, to a smaller extent, in the Zeilanite from Iserwiese. (G. Rose, *Pogg.* 50, 652.

	At.	*Chlorospinelle.*		G. Rose.	At.			G. Rose.
CaO				0·27				
MgO	12	240·0	27·17	26·77	7	140·0	26·60	27·49
CuO				0·27				0·52
Fe^2O^3	1	78·0	8·83	8·70	1	78·0	14·82	14·77
Al^2O^3	11	565·4	64·00	64·13	6	308·4	58·58	57·34
		883·4	100·00	100·14		526·4	100·02	100·12

¶ Ebelmen, by exposing a mixture of 3·30 pts. alumina, 2·57 ferric oxide, and 2·50 boracic acid, to the heat of a pottery furnace, obtained a mass, the whole surface of which was covered with intersecting

light brown, transparent or translucent laminæ; they were hard enough to scratch quartz. The compound Al^2O^3,FeO has lately been discovered by Lippe, and named *Hencinite*. (*Ann. Pharm.* 68, 266.) ¶

C. Carbide of Iron and Aluminum.—Formed by raising an intimate mixture of alumina and carbide of iron *d.* (p. 219) to an intense white heat.—Very brittle and white; yields by analysis, 6·4 p. c. alumina. When fused with 15 parts of steel, it forms an alloy resembling Indian steel. (Faraday & Stodart.)

D. Sulphate of Alumina and Ferrous Oxide.—*a. A species of Feather-salt.*—Formed by the weathering of iron-pyrites diffused through slate-clay in the abandoned mines of Hurlet and Campsie.—Asbestus-like mass, consisting of colourless, silky fibres, which turn brown in moist air, are easily soluble in water, on the evaporation of which, crystals of green vitriol separate out, the alumina remaining in the mother-liquid. (Phillips, *Ann. Phil.* 21, 446.)

					Phillips.
$6FeO$	210·0	....	20·72	.....	20·7
Al^2O^3	51·4	....	5·07	.....	5·2
$8SO^3$	320·0	....	31·58	.....	30·9
$48HO$	432·0	....	42·63	.....	43·2
$6(FeO,SO^3)+Al^2O^3,2SO^3+48Aq.$	1013·4	....	100·00	.....	100·0

b. Another kind of Feather-salt.—White, silky, asbestus-like bundles of fibres, which have a styptic taste, give off water when gently heated, fuse readily, and dissolve perfectly in water, forming a colourless solution. Origin unknown. (Berthier, *Schw.* 33, 472.)—A similar composition is that of *Mountain-butter*, which occurs at Wetzelsteir near Saalfeld in white, botrymous, and kidney-shaped masses. (Brandes, *Schw.* 39, 417.)

					Berthier. *Feather-salt.*		Brandes. *Mountain-butter.*
NH^3		....		....		....	1·78
NaO		....		....		....	0·72
MgO		....		....	0·8	....	0·81
$2FeO$	70·0	....	12·40	....	12·0	....	10·12
Al^2O^3	51·4	....	9·11	....	8·8	....	7·11
$5SO^3$	200·0	....	35·44	....	34·4	....	35·33
$27HO$	243·0	....	43·05	....	44·0	....	44·13
$2(FeO,SO^3)+Al^2O^3,3SO^3+27Aq.$	564·4	....	100·00	....	100·0	....	100·00

c. Another kind of Feather-salt, corresponding in composition to alum. From the quicksilver mine at Mörsfeld. Yellowish-white, silky mass, consisting of soft parallel fibres. (Rammelsberg, *Pogg.* 43, 399.)—The same salt is obtained artificially by mixing the solutions of green vitriol and sulphate of alumina with a large excess of sulphuric acid. The mixture, when put into a porcelain basin with rough sides, and left to evaporate in a warm place, effloresces in long, silky threads, united in bundles, which are very apt to creep over the edge of the vessel. (Klauer, *Ann. Pharm.* 14, 261.)

hydrofluosilicic acid, the silicium being oxidated. When exposed to the air in a moist state, it is converted into a rusty yellow-ochre. (Berzelius.)

B. Silicate of Ferrous Oxide, or Ferrous Silicate.—*a. Disilicate.*—Often produced in the conversion of cast into wrought iron, and in the refining of coarse copper; in the latter case, it is mixed with the sulphides of copper and iron. Exhibits the same crystalline form with the same cleavage-planes, likewise the same lustre and hardness as Chrysolite (III., 395) even when disilicate of lime is mixed with it. Hydrochloric acid extracts the ferrous oxide, and leaves the silica (in the form of a jelly: *Kobell*) undissolved. (Mitscherlich, *Ann. Chim. Phys.* 24, 359; Walchner, *Schw.* 39, 71; *comp.* Miller, *Pogg.* 23, 559.)

			Mitscherlich.			Walchner.		
			a.	*b.*		*c.*	*d.*	*e.*
KO						0·20	0·29	0·19
MgO			0·65			1·90	1·41	1·31
MnO						1·30	2·65	1·46
2FeO	70	69·31	67·24	69·07	Fe^2O^3	61·23	62·04	63·32
CuO								2·65
Al^2O^3						1·56		1·25
SiO^2	31	30·69	31·16	30·93		32·96	32·35	29·25
	101	100·00	99·05	100·00		99·15	98·74	99·43

a. are crystals from iron-works; *b.* from the copper-refinery; the admixed sulphide of iron and sulphide of copper have been allowed for in the analysis; *c.* from the iron-works at Dax in the Pyrenees, sp. gr. 3·7; *d.* from the iron-works at Bodenhausen in the Harz; very much like hyalosiderite, sp. gr. 3·529; *e.* from the copper-refinery at Lauterthal in the Harz, sp. gr. 3·87.

To this head belong also *Hyalosiderite* and *Fayalite*, excepting that a large quantity of the ferrous oxide is replaced by magnesia and other bases. *Hyalosiderite* has the form of chrysolite; sp. gr. 2·875; harder than apatite, yellowish-brown; translucent at the edges, where it exhibits a hyacinth-red colour. If not naturally magnetic, it becomes so when heated to redness, when it also turns black; at a higher temperature, it fuses to a black magnetic globule. With borax or microcosmic salt, it gives the reactions of iron, and with microcosmic salt, immediately a skeleton of silica. It dissolves with difficulty in cold, concentrated hydrochloric acid, and yields a jelly on evaporation. (Walchner, *Schw.* 39, 65.)—*Fayalite* is sometimes of crystalline structure, sometimes fused and blistered; sp. gr. 4·138; softer than quartz, greenish-black, and strongly attracted by the magnet. Fuses very easily and quietly to a metallic globule, with evolution of sulphurous acid; dissolves readily in borax and in microcosmic salt. Strong-fuming nitric acid converts it into a jelly; but when this jelly, after washing with water, is boiled with carbonate of potash, which dissolves the gelatinous silica, there remains another mineral, insoluble even in boiling oil of vitriol; this latter mineral was therefore intimately mixed with the soluble mineral, the purer Fayalite. (C. G. Gmelin, *Pogg.* 51, 160.)

	Hyalosiderite.				Walchner.
KO		....		.....	2·79
4MgO	80	....	32·92	.....	32·40
MnO		....		.....	0·48
2FeO	70	....	28·80	.....	29·71
$3SiO^2$	93	....	38·28	.....	31·64
Al^2O^3		....		.....	2·21
Cr^2O^3		....		.....	trace
	243	....	100·00	.....	99·23

	Soluble part of Fayalite.				C. G. Gmelin.		Fellenberg.
CaO		....		.....		....	0·43
MnO		....		.....	2·94	....	0·79
2FeO	70	....	69·31	.....	65·84	....	62·57
CuO		....		.....	0·60	....	0·32
PbO		....		.....		....	1·71
$1SiO^2$	31	....	30·69	.....	24·93	....	31·04
Al^2O^3		....		.....	1·84	....	3·27
FeS		....		.....	2·77		
S and Cl		....		.....		....	trace
	101	....	100·00	.....	98·92	....	100·13

In Walchner's analysis, the 29·71 denotes not ferrous but ferroso-ferric oxide.—The insoluble portion of Fayalite exhibits such diversities of composition that it cannot be reduced to calculation.

Knebelite.—FeO, MnO, SiO^2.—Decomposed by hydrochloric acid, with separation of gelatinous silica. (Döbereiner, *Schw.* 21, 41.)

	Knebelite.				Döbereiner.
MnO	36	....	35·30	.....	35·0
FeO	35	....	34·31	.....	32·0
SiO^2	31	....	30·39	.....	32·5
	102	....	100·00	.....	99·5

b. Monosilicate.—*α.* Sometimes found in the slag of the blast-furnaces (partly mixed with monosilicate of lime) in greenish, often transparent crystals corresponding to those of Augite. (Mitscherlich.)

When a mixture of 1 At. SiO^2 and 1 At. Fe^2O^3 is fused for an hour in a charcoal crucible, iron is reduced, and a slag (*a*) formed, resembling the slag produced towards the end of the process of converting cast into wrought-iron; composition = FeO, SiO^2 nearly. The iron reduced in the process is not pig-iron, but very malleable, partly of specific gravity 8·089; the ferrous silicate appears therefore to prevent the combination of carbon and silicium with the iron.—By fusion for several hours in a blast-furnace, more iron is reduced from the slag, likewise malleable and containing only 0·59 per cent. of carbon, together with a trace of silicium; and the slag *b* has very nearly the composition $2FeO,3SiO^2$. (Sefström, *J. techn. Chim.* 10, 178.)

	Slag a.				Sefström.		*Slag b.*				Sefström.
FeO	35	....	53·03	....	51·2	$2FeO$	70	....	42·94	....	46·05
SiO^2	31	....	46·97	....	49·6	$3SiO^2$	93	....	57·06	....	53·95
FeO,SiO^2	66	....	100·00	....	100·8	$2FeO,3SiO^2$	163	....	100·00	....	100·00

Pyrosmalite.—$15(MnO, SiO^2) + 15(FeO,SiO^2) + Fe^2Cl^3, 3Fe^2O^3, 3Aq.$? —Regular six-sided prisms, the lateral edges twice truncated. Cleavage

perpendicular to the axis; less distinct parallel to the lateral faces. Sp. gr. 3·081; yellowish-brown without, greenish-yellow within; opaque; yields a light green powder. Before the blowpipe it assumes a black-brown colour, gives off vapours of water, hydrochloric acid, and sesquichloride of iron, and fuses to a black magnetic globule. Dissolves readily in borax, exhibiting the reactions of manganese and iron—with difficulty in microcosmic salt. Dissolves in nitric acid with separation of silica. (Hisinger, *Schw.* 23, 63.) Hydrochloric acid, after long digestion, decomposes it completely, without forming a siliceous jelly. (H. Rose.)

					Hisinger.
CaO					1·21
15MnO	540·0		22·35		23·45
15FeO	525·0		21·73		20·78 *
$30SiO^2$	930·0		38·49		35·85
$4Fe^2O^3$	312·0		12·91		12·34 *
3(Cl—O)	82·2		3·40		2·91
3HO	27·0		1·12		undetermined
	2416·2		100·00		

c. Six-fifths Silicate.—Hornblendes rich in Iron.—α. Arfvedsonite. 5(NaO; CaO; MgO; MnO; FeO). $6SiO^2$.—$u' : u = 123° 55'$. Fuses even in the flame of a candle; boils up strongly before the blowpipe, and yields a black magnetic globule. Not soluble in acids or in caustic potash. (v. Kobell, *J. pr. Chem.* 13, 3.)

	At.						Kobell. From Greenland.
NaO	4		124·8		8·77		8·00
CaO	1		28·0		1·97		1·50
MgO							0·42
MnO							0·62
FeO	15		525·0		36·93		36·12
SiO^2	24		744·0		52·33		49·27
Al^2O^3							2·00
Cl							0·24
			1421·8		100·00		98·17

β. Aegyrine.—5(KO; NaO; CaO; MgO; MnO; FeO), 6 SiO^2.—Resembles hornblende in outward appearance. Fuses to a black globule; forms a green transparent bead with a large quantity of borax, and a black bead with a still larger quantity. With microcosmic salt it forms a green glass and a skeleton of silica. Dissolves abundantly in carbonate of soda, forming a brown opaque bead. Contains titaniferous iron injected into it. (Plantamour, *J. pr. Chem.* 24, 300.)

* Hisinger found, on the whole, 35·48 p.c. sesquioxide of iron, of which, however, he supposed that the greater part was contained in the mineral in the form of protoxide. In the above calculation, $\frac{14}{23}$ of the sesquioxide found by Hisinger is reckoned as protoxide, and the remaining $\frac{9}{23}$ as sesquioxide.

					Kersten.
Mn^2O^3	80	24·32	25·01	to	26·54
Fe^2O^3	78	24·01	22·90	„	21·00
$2SiO^2$	62	18·84	18·98	„	18·07
12HO	108	32·83	33·00	„	32·82
	328	100·00	99·89	„	98·43

b. Sesquisilicate.—Yellow Earth from Amberg.—$2(Fe^2O^3; Al^2O^3)$, $3SiO^2 + 4$ Aq. (Kühn, *Schw.* 51, 466.)

	Yellow Earth.			Kühn.
MgO				1·38
$5Fe^2O^3$	390·0	36·79		37·76
$3Al^2O^3$	154·2	14·54		14·21
$12SiO^2$	372·0	35·09		33·23
16HO	144·0	13·58		13·24
	1060·2	100·00		99·82

c. Bisilicate.—Hisingerite.—Fe^2O^3, $2SiO^2 + 4$ Aq.—Amorphous, with an uneven, conchoidal fracture. Black, but produces a yellowish-brown powder Gives off water when heated; the blowpipe-flame rounds it off at the edges, and renders it dull and magnetic. (Hisinger, *Pogg.* 13, 505.) Hydrochloric acid decomposes it, with formation of gelatinous silica. In the analysis of Hisingerite from Bodenmais (also called *Thraulite*), the admixed magnetic pyrites was deducted by Hisinger, and likewise by Kobell. (*Pogg.* 14, 467; *Schw.* 62, 198.)

	Hisingerite.			Hisinger. Riddarhyttan.	Hisinger. Bodenmais.	Kobell. Bodenmais.
Fe^2O^3	78	44·32		45·95	51·53	50·86
$2SiO^2$	62	35·23		36·30	31·78	31·28
4HO	36	20·45		20·70	20·00	19·12
	176	100·00		102·95	103·31	101·26

In the mineral from Riddarhyttan, Hisinger found 44·39 per cent., and in that from Bodenmais, 49·87 per cent. of Fe^3O^4, which, in the above analyses is reckoned as Fe^2O^3. Kobell found in the mineral from Bodenmais, 5·7 per cent. of FeO, which, however, he supposed to arise from the presence of magnetic pyrites. This perhaps is the origin of the excess of ferric oxide over the silica, which is apparent in the analyses; or, on the other hand, this excess may arise from the actual composition of Hisingerite: if that be the case, the mineral may perhaps be represented by the formula:—$2Fe^2O^3$, $3SiO^2 + 4$ Aq, analogous to *Yellow Earth.*

The *Ochre* which is deposited by the hot spring at Lucca on exposure to the air, probably from ferrous silicate contained in it, and which dissolves in hydrochloric acid with separation of gelatinous silica, contains [besides water?] 57·17 p. c. ferric oxide to 42·86 silica. (H. Davy, *Schw.* 35, 78.) [Fe^2O^3, $2SiO^2$ requires 55·71 p. c. ferric oxide to 44·29 silica.]

d. Tersilicate.—Nontronite.—Fe^2O^3,$3SiO^2 + 5$Aq.—Massive, with a splintery or earthy fracture; translucent or opaque; varies in colour from siskin-green to straw-yellow. When immersed in water, it gives off bubbles and becomes transparent. Before the blowpipe it decrepitates, turns yellow, then brown, then black, and acquires magnetic properties, but without fusing. Insoluble in cold acids, but soluble in hot sulphuric, hydrochloric, or nitric acid, with separation of gelatinous silica. (Berthier,

(*Ann. Chim. Phys.* 36, 22; Jacquelain, *Ann. Chim. Phys.* 66, 101; Bieward, *J. pr. Chem.* 11, 162.)

	At.	*Nontronite.*		Berthier. St. Pardoux.	Jacquelain. Montmort.	Biewend. Andreasberg.
CaO					0·19	trace
MgO				2·1		
MnO						trace
ZnO					trace	
CuO					0·90	
Fe^2O^3	1	78	36·11	29·0	35·69	37·30
Al^2O^3				3·6	3·31	
SiO^2	3	93	43·06	44·0	41·31	41·10
HO	5	45	20·83	18·7	18·63	21·56
Clay				1·2		
		216	100·00	98·6	100·00	99·96

e. Quadrosilicate.—Anthosiderite.—Fe^2O^3, $4SiO^2 + Aq$?—Composed of soft fibres; sp. gr. about 3·0; gives sparks with steel; ochre-brown, translucent in thin fragments. (Hausmann & Schnedermann, *Pogg.* 52, 292.)

	Anthosiderite.		Schnedermann.
Fe^2O^3	78	36·97	34·99
$4SiO$	124	58·77	60·08
HO	9	4·26	3·59
	211	100·00	98·66

When quadrosilicate of soda is gradually added to hydrochlorate of ferric oxide, the precipitate, as it forms, is immediately re-dissolved, with the exception of a small quantity of silica, and the liquid acquires a dark colour. On evaporating the liquid, a red-brown mass is left, translucent at the edges, and exhibiting a conchoidal fracture. Water causes it to decrepitate, and extracts from it chloride of sodium, together with the excess of ferric chloride, while ferric silicate is left behind in the form of a light yellowish-brown powder, from which hydrochloric acid extracts the whole of the ferric oxide.—With excess of tersulphate of ferric oxide, quadrosilicate of soda gives a precipitate only on boiling, but if the latter salt is in excess, the mixture solidifies in 24 hours. (Walcker, *N. Quart. J. of Sc.* 3, 371.)

Silicate of Ferric Oxide with Carbonate of Potash.—Bibasic.—Glauber's Iron-tree.—When a piece of perfectly dry protochloride of iron is immersed in soluble silica (obtained by fusing 1 pt. quartz and 3 pts. carbonate of potash, and dissolving the fused mass in water) thin, white, ribbon-shaped and thread-like columns or branches immediately rise from it to the surface of the liquid, and there form a kind of canopy; their colour is first green, and then brown, and they may be preserved if the liquid be carefully poured off from them. (R. Böttger, *J. pr. Chem.* 10, 60.)—Protochloride of iron forms white branches which rise perpendicularly, and after awhile turn green, then black, and lastly red by oxidation. Sesquichloride of iron forms red branches. Green and blue vitriol likewise form trees. At the top of each branch is situated a gas-bubble, which, as it rises through the liquid, carries the iron-salt along with it. If the gas-bubble be removed, the growth of the branch is arrested. A large gas-bubble produces a thick, hollow branch terminating in a hemispherical summit. If a fresh gas-bubble carries an

additional quantity of iron-salt up through the hollow tube, the bubble then breaks through the summit and fills the whole liquid with crooked threads which spread out into a globe filled with gas. In the following table, *a.* gives the composition of the iron-tree obtained with protochloride of iron previously heated till it began to turn red; *b.* that formed by protochloride which had remained white; and *c.* that produced by the sesquichloride, after previous trituration and washing with water. (Mulder, *J. pr. Chem.* 22, 41.)

				Mulder.		
				a.	*b.*	*c.*
$6Fe^2O^3$	468·0	66·91		67·0	67·2	66·7
$3SiO^2$	93·0	13·30		12·7	13·7	13·8
$2KO$	94·4	13·50		13·7		14·7
$2CO^2$	44·0	6·29		6·6		4·8
$3(2Fe^2O^3,SiO^2)+2(KO,CO^2)$	699·4	100·00		100·0		100·0

The carbonic acid was determined merely by loss. Mulder regards the compound as silicate of potash combined with carbonate of ferric oxide.

b. With 4 *At. acid.*—The precipitate formed with solution of silica and hydrochlorate of ferric oxide contains 25·3 p. c. ferric oxide, 45·3 silica, 21·1 potash, and 9·9 carbonic acid. (Mulder.)

Double Silicates containing Ferric Oxide and Alumina on the one hand, and Ferrous Oxide and others of the stronger bases on the other.

Chamoisite.—$2(5FeO,SiO^2)+Al^2O^3,3SiO^2+12Aq$.—Massive; fracture granular, uneven, or earthy; sp. gr. from 3·0 to 3·4; dark greenish-grey; magnetic. When heated, it gives off water, becomes more strongly magnetic and turns black, or if the air has access to it, reddish. Dissolves readily in hydrochloric acid with separation of gelatinous silica, blackened by asphalt. (Berthier, *Schw.* 33, 345.)

	Chamoisite.		Berthier. From Chamoisin.
$10FeO$	350·0	58·10	60·5
Al^2O^3	51·4	8·53	7·8
$3SiO^2$	93·0	15·44	14·3
$12HO$	108·0	17·93	17·4
	602·4	100·00	100·0

Pea-ore or *Lenticular Grey Iron-stone* from the Albinger pit near Kanderne.—$10FeO,3SiO^2+Al^2O^3,SiO^2+5Aq$?—Nodules having a diameter varying from 1 line to 2 inches, splitting off in thin scales; sp. gr. 3·1; dingy olive-green inclining to yellow. Dissolves slowly but completely in aqua-regia, and yields gelatinous silica when evaporated. (Walchner, *Schw.* 51, 219.)

	Pea-ore.			Walchner.		
CaO and MnO				trace		trace
$10FeO$	350·0	61·36		61·61	,,	62·44
Al^2O^3	51·4	9·01		8·58	,,	8·46
$4SiO^2$	124·0	21·74		20·85	,,	21·66
$5HO$	45·0	7·89		8·18	,,	7·92
	570·4	100·00		99·22	,,	100·48

Simpler, but less in accordance with the analysis is the formula $3(3FeO,SiO^2)+Al^2O^3,SiO^2+5Aq$.

Stilpnomelane—$9(FeO,SiO^2)+Al^2O^3,3SiO^2+7Aq$.—Laminar; sp. gr. from 3·0 to 3·4; lustrous, raven-black, yields a greenish-black powder. Gives off ammoniacal water when heated; fuses with difficulty before the blowpipe, into a black, shining globule; gives the manganese reaction with carbonate of soda; dissolves completely in borax, exhibiting the iron reaction, and in microcosmic salt, with separation of a siliceous jelly. Dissolves but incompletely in hydrochloric acid even when warm and concentrated. (Rammelsberg, *Pogg.* 43, 127.)

	Stilpnomelane.				Rammelsberg (*mean*).
KO, with trace of NaO		....		.....	0·75
CaO		....		.....	0·52
MgO	20·0	....	2·54	.....	2·39
8FeO	280·0	....	35·60	.....	36·04
Al^2O^3	51·4	....	6·54	.....	6·75
$12SiO^2$	372·0	....	47·31	.....	45·02
7HO	63·0	....	8·01	.....	7·96
	786·4	....	100·00	.....	99·43

Gedrite.—$8FeO,6SiO^2+Al^2O^3,SiO^2+Aq$?—Fibrous, somewhat laminar; sp. gr. 3·26; violet-brown, with semi-metallic lustre. Fuses readily to a black slag; forms a blackish-green glass with borax. Not attacked by acids. (Dufrénoy, *J. pr. Chem.* 11, 132.)

	Gedrite.				Dufrénoy.
CaO		....		.....	0·67
MgO	20·0	....	3·69	.....	4·13
7FeO	245·0	....	45·17	.....	45·83
Al^2O^3	51·4	....	9·47	.....	9·31
$7SiO^2$	217·0	....	40·01	.....	38·81
HO	9·0	....	1·66	.....	2·30
	542·4	....	100·00	.....	101·05

Ilvaite.—$2(2FeO,SiO^2)+Fe^2O^3,SiO^2$; or more exactly, $4(2FeO,SiO^2)+2(2CaO,SiO^2)+3(Fe^2O^3,SiO^2)$.—Crystalline system the right prismatic. *Fig.* 54, 62 (without the *p*-face), and other forms; $u' : u$ (*Fig.* 62)$=112° 36'$; $\alpha : u=128° 29'$. (Hauy.) Sp. gr. 3·9 to 4·0; harder than apatite; opaque, with semi-metallic lustre; greyish-black. Fuses easily before the blowpipe, and forms a black magnetic bead. Dissolves with the iron reaction in borax and in microcosmic salt, in the latter with separation of a siliceous skeleton. Dissolves easily and completely in warm hydrochloric acid, forming a jelly.

	At.		*Ilvaite.*				Stromeyer.		Rammelsberg. (*mean*).
CaO	4	....	112	....	12·37	.....	13·78	....	11·26
MnO		....		....		.....	1·59	....	1·51
FeO	8	....	280	....	30·94	.....	31·90	....	32·63
Fe^2O^3	3	....	234	....	25·86	.....	23·00	....	22·78
Al^2O^3		....		....		.....	0·61		
SiO^2	9	....	279	....	30·83	.....	29·28	....	29·46
HO		....		....		.....	1·27	....	1·60
			905	....	100·00	.....	101·43	....	99·24

In Stromeyer's original analysis, the whole of the iron was estimated as protoxide, which amounted to 52·14 per cent. Kobell found that the mineral contained 23 per cent. of ferric oxide, and Stromeyer's analysis, given in the preceding table, is calculated accordingly.

Cronstedtite.—$3FeO, SiO^2 + Fe^2O^3, SiO^2 + 3Aq$?—Regular six-sided prisms (*Fig.* 135); cleavage very distinct parallel to *p*, less distinct parallel to *s*; sp. gr. = 3·348; softer than calcspar; opaque, raven-black, powder greyish-green; non-magnetic. Before the blowpipe, it froths a little, without melting; but in the oxy-hydrogen flame, it melts to a black-brown globule; with borax it forms a black bead. Dissolves readily in dilute sulphuric or hydrochloric acid, forming a solution which becomes gelatinous. (Steinmann, *Schw.* 32, 69.)

	At.	*Constredtite.*		Steinmann. Exp. 1.	Steinmann. Exp. 2.	Kobell.
MgO	1	20	3·78	5·08	3·25	
MnO				2·89	3·82	
FeO	5	175	33·08	58·85	57·61	27·11
Fe^2O^3	2	156	29·49			35·36
SiO^2	4	124	23·44	22·45	22·83	
HO	6	54	10·21	10·70	10·70	
		529	100·00	99·97	98·21	

Steinmann calculated all the iron as protoxide. Kobell found 35·35 p. c. ferric oxide, according to which, in Steinmann's first analysis, there remains 27·11 ferrous oxide.

Wichtyn.—$3(FeO, SiO^2) + Al^2O^3, 3SiO^2$; or more completely, $3(NaO; CaO; MgO; FeO), 3SiO^2 + 1(Al^2O^3, Fe^2O^3), 3SiO^2$.—Its composition is therefore analogous to that of felspar. It has two cleavage-planes which cut one another almost at a right angle; sp. gr. 3·03; scratches glass; black. Forms a black bead before the blowpipe, and a bottle-green glass with borax. Not attacked by hydrochloric acid. (Laurent, *Ann. Chim. Phys.* 59, 109.)

	Wichtyn.		Laurent.
2NaO	62·4	3·13	3·5
5CaO	140·0	7·02	6·0
3MgO	60·0	3·01	3·0
8FeO	280·0	14·05	13·0
Fe^2O^3	78·0	3·92	4·0
$5Al^2O^3$	257·0	12·88	13·3
$36SiO^2$	1116·0	55·99	56·3
	1993·4	100·00	99·1

Achmite.—$NaO, 2SiO^2 + FeO, SiO^2 + Fe^2O^3, 3SiO^2$?—Crystalline system the right prismatic. *Fig.* 66, but without the *y*-faces, and without the small faces between *a* and *t*; the acumination is likewise much sharper. $u : u' = 86° 56'$; $u : t = 133° 28'$; $u : m = 136° 32'$. (Mitscherlich.) Cleavage parallel to *u*, less distinct parallel to *m* and *t*. Sp. gr. 3·24; scratches glass. In thin fragments it is translucent and exhibits a yellowish-brown colour; on the outside it is brown-black or red-brown; blackish or dark greyish-green on the fractured surfaces. Before the blowpipe, it fuses into a black bead. (Ström, *Schw.* 37, 201.)

	At.	*Achmite.*		Ström.	Berzelius.	Kobell.
NaO	1	31·2	9·45	9·74	10·40	
CaO					0·72	
MnO					1·08	
FeO	1	35·0	10·60			
Fe^2O^3	1	78·0	23·62	34·44	31·25	
SiO^2	6	186·0	56·33	54·27	55·25	
TiO^2				trace	trace	3·25
Water				1·88		
		330·2	100·00	100·33	98·70	

Ström and Berzelius assume that all the iron in Achmite is in the state of ferric oxide; but according to Kobell, the greater portion is in the state of ferrous oxide.

Ottrelite.—$3(FeO,SiO^2)+2Al^2O^3,3SiO^2+3Aq$.—Fuses with difficulty in the blowpipe flame at the edges, yielding a black magnetic glass. When fused with carbonate of soda, it exhibits the manganese reaction, and with borax the iron reaction. Not decomposed by any acid except heated sulphuric acid. (Damour.)

	Ottrelite.				Damour. From Ottrez.		
MnO	36·0	....	8·54	.....	8·03	to	8·18
2FeO	70·0	....	16·59	.....	16·81	,,	16·72
$2Al^2O^3$	102·8	....	24·37	.....	23·89	,,	24·63
$6SiO^2$	186·0	....	44·10	.....	43·52	,,	43·34
3HO	27·0	....	6·40	.....	5·63	,,	5·66
	421·8	....	100·00	.....	97·88	,,	98·53

Chlorite-spar.—$2FeO,SiO^2+2Al^2O^3,SiO^2$. — Becomes darker before the blowpipe, and afterwards red-brown, but without fusing; exhibits traces of manganese when fused with carbonate of soda. Dissolves in borax forming a dark green bead. Microcosmic salt dissolves it slowly but completely, without leaving a siliceous skeleton, and forms with it a glass coloured by iron while hot, but colourless when cold. Not soluble in hydrochloric acid. Hence the mineral, previously to analysis, may be freed from ferric oxide and alumina by digestion in hydrochloric acid. (Erdmann, *J. pr. Chem.* 6, 89.)

	Chlorite-spar.				Erdmann. From Kosoibrod.
2FeO	70·0	....	29·81	.....	30·05
$2Al^2O^3$	102·8	....	43·78	.....	45·02
$2SiO^2$	62·0	....	26·41	.....	24·93
	234·8	....	100·00	.....	100·00

Lepidomelane. — $(KO; FeO), SiO^2 + (Fe^2O^3; Al^2O^3), SiO^2$; or more exactly: $4(KO, SiO^3)+7(FeO, SiO^2)+7(Fe^2O^3, SiO^2)+4(Al^2O^3, SiO^2)$.—Raven-black, shining, opaque, micaceous, crystalline scales, united in granulo-laminar masses: sp. gr. 3·00. Before the blowpipe it acquires a pinchbeck-brown colour, and fuses to a black magnetic bead; dissolves in borax, forming a green glass. Hydrochloric acid dissolves it, with separation of silica in the form of the crystalline scales of the mineral. (Wöhler & Soltmann, *Pogg.* 50, 664.)

	At.		*Lepidomelane.*				Soltmann.
KO	4	....	188·8	....	10·11	.....	9·20
CaO, MgO		....		....		.....	0·26
FeO	7	....	245·0	....	13·12	.....	12·43
Fe^2O^3	7	....	546·0	....	29·19	.....	27·66
Al^2O^3	4	....	205·6	....	11·01	.....	11·60
SiO^2	22	....	682·0	....	36·57	.....	37·40
HO		....		....		.....	0·60
			1867·4	....	100·00	.....	99·15

Pinguite.—$FeO,2SiO^2+2(Fe^2O^3, 2SiO^2)+14Aq$?—Resembles Bole. Fracture, conchoido-splintry; sp. gr. 2·315. Very soft; greasy to the touch; does not become softer by immersion in water. Has a faint waxy lustre, and a siskin-green colour. (Breithaupt, *Schw.* 55, 303.)

When heated, it gives off water and becomes black-brown; before the blowpipe it fuses at the edges only. With carbonate of soda it fuses to a black slag. Dissolves in borax, exhibiting the iron reaction, and in microcosmic salt, with separation of a skeleton of silica. Warm hydrochloric acid decomposes it readily, with separation of pulverulent silica, which does not lose the greenish colour of the mineral till it has been digested with hydrochloric acid for a considerable time. (Karsten, *Schw.* 66, 9.)

	At.		*Pinguite.*				Karsten. Wolkenstein.
CaO							
MgO							0·45
Mn^2O^3							0·15
FeO	1		35		6·96		6·10
Fe^2O^3	2		156		31·01		29·50
Al^2O^3							1·80
SiO^2	6		186		36·98		36·90
HO	14		126		25·05		25·10
			503		100·00		100·00

Glass-fluxes containing Ferrous and Ferric Oxide.—Ferrous oxide imparts a bottle-green colour to glass. Glass coloured with ferric oxide is blood-red while hot, yellowish after cooling.

D. Carbide of Silicium and Iron.—Berzelius (*Gilb.* 36, 89) and Stromeyer (*Gilb.* 38, 321) obtained this compound by heating a mixture of silica, iron and lamp-black to intense whiteness.—Stromeyer obtained five varieties: *a.* Platinum-coloured, lamino-granular, superficially crystalline, brittle.—*b.* Tin-white, having the texture of cast-iron, brittle.—*c.* Silver-white, compact and granular, brittle.—*d.* Steel-coloured, susceptible of polish, as hard as steel, of coarse steel-like texture, subductile.—*e.* Steel-coloured, susceptible of polish, as hard as steel, very fine-grained, perfectly ductile.—The densities of these varieties were between 6·8 and 7·3 inclusive.—Berzelius obtained an alloy, which, when dissolved in hydrochloric acid, yielded 19 per cent. of silica, and yet was malleable and very soft.

	a.		*b.*		*c.*		*d.*		*e.*
Fe	85·3		87·4		91·2		95·2		96·2
Si	9·3		8·0		5·7		3·0		2·2
C	5·4		4·6		3·1		1·8		1·6
	100·0		100·0		100·0		100·0		100·0

Acids dissolve the iron and leave a black substance of unaltered form, which turns white on ignition in the air, and if then again treated with acids, gives up a fresh portion of iron, previously enveloped in the carbon. The ultimate residue consists of gelatinous silica. (Stromeyer.)

E. Protofluoride of Iron and Silicium.—FeF,SiF^2.—Formed when a solution of iron in hydrofluosilicic acid is left to evaporate in an iron dish and exposed to the air. Pale bluish-green, regular six-sided prisms, which may be derived from a rhombohedron. Easily soluble in water. (Berzelius.)

F. Sesquifluoride of Iron and Silicium.—$Fe^2F^3,3SiF^2$.—The *slightly coloured* solution of hydrated ferric oxide in terhydrofluate of

	At.						H. Rose. b.		Mosander. c.
CaO		....		....		.....		....	0·96
MgO		....		....		.....		....	2·30
MnO		....		....		.....		....	0·21
FeO	6	....	210	....	39·77	.....	42·70	....	27·23
TiO^2	6	....	240	....	45·46	.....	43·73	....	39·04
Fe^2O^3	1	....	78	....	14·77	.....	13·57	....	29·16
Cr^2O^3		....		....		.....		....	0·12
SiO^2		....		....		.....		....	0·31
			528	....	100·00	.....	100·00	....	99·33

a. is Ilmenite, from the Ilmengebirg.—*b.* Titaniferous Iron from Egersund.—*c.* the same; sp. gr. 4·745; magnetic here and there; rounding off at the edges in the blowpipe-flame; composed of $3(FeO,TiO^2)+Fe^2O^3$, nearly:

	At.						Mosander. a.
CaO		....		....		.....	0·33
MgO		....		....		.....	0·68
FeO	1	....	35	....	22·87	.....	19·91
TiO^2	1	....	40	....	26·14	.....	24·19
Fe^2O^3	1	....	78	....	50·99	.....	53·01
SiO^2		....		....		.....	1·17
			153	....	100·00	.....	99·29

	At.						Kobell. b.		Plantamour. c.
MgO		....		....		.....	0·80		
FeO	2	....	70	....	12·96	.....	10·04	....	11·32
TiO^2	2	....	80	....	14·82	.....	14·16	....	15·56
Fe^2O^3	3	....	390	....	72·22	.....	75·00	....	71·25
SiO^2		....		....		.....		....	1·87*
			540	....	100·00	.....	100·00	....	100·00

a. is Titaniferous Iron from Arendal, only partly magnetic.—*b.* Titaniferous Iron from the Spessart. Sp. gr. 4·78; magnetically attractive in lumps, but, in the state of powder, it is not even attracted by the magnet.—*c.* is Titaniferous Iron from Uddevalla, slightly magnetic; when urged by a strong blast, it fuses into a steel-grey bead, the ferric oxide being reduced to ferroso-ferric oxide. When ignited in a current of hydrogen gas, it gives off 24·55 p. c. oxygen, with traces of fluoride of silicium: the number 1·87 under *c.* in the last table includes fluorine and loss, besides silica.

Crichtonite appears also to be allied to Ilmenite.

β. *Kibdelophane*, or *Titaniferous Iron from Gastein.*—Crystals having the form of Iron-glance and Ilmenite; *Fig.* 151; $r^3 : r^5 = 86°$; $r^1 : r^3$ or $r^5 = 94°$. Cleavage parallel to *p*, less distinct parallel to *r*. Hardness between fluorspar and felspar. Sp. gr. 4·66. Slightly magnetic. (Mohs.) It is remarkable that FeO,TiO^2 and $2FeO,3TiO^2$ should exhibit the same crystalline form. (Kobell, *Schw.* 64, 245.)

	At.		*Kibdelophane.*				Kobell.
MnO		....		....		.....	1·65
FeO	14	....	490	....	34·80	.....	36·00
TiO^2	21	....	840	....	59·66	.....	59·00
Fe^2O^3	1	....	78	....	5·54	.....	4·25
			1408	....	100·00	.....	100·90

γ. *Basanomelane*, or the *Iron-roses* (*Eisenrosen*) from Switzerland.

	At.	*Basanomelane.*		Kobell.
FeO	1	35	4·73	5·01
TiO^2	2	80	10·83	9·66
Fe^2O^3	8	624	84·44	85·33
		739	100·00	100·00

Analyses of titaniferous iron, which do not admit of stoïchometric calculation, because the proportion of protoxide to sesquioxide of iron in them has not been correctly determined.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*
MnO	4·5	1·6	2·6	0·5	1·00	
$FeO + Fe^2O^3$	82·0	79·2	79·0	85·5	63·74	72
TiO^2	12·6	14·8	15·9	14·0	33·00	28
Al^2O^3	0·6	0·8	1·0		2·00	
	99·7	96·4	98·5	100·0	99·74	100

	g.	*h.*	*i.*	*k.*
MnO			0·25	2
$FeO + Fe^2O^3$	49·88	49	51·00	14
TiO^2	50·12	40	45·25	84
SiO^2			3·50	
Al^2O^3		11		
	100·00	100	100·00	100

a. *Titaniferous Iron* from Puy à Velay. (Cordier.)

b. From Teneriffe. (Cordier.)

c. From Niedermennich. (Cordier.) *a.* to *c.*, octohedral.

d. From the sea-sand of the coast of Finland. Attracted by the magnet. Sp. gr. 4·545. (Klaproth.)

e. From the sea-sand at Warnemünde on the Baltic. Attracted by the magnet. Sp. gr. 3·153 [?] (Möhl.)

f. *Iserine*, from the Vale of the Iser. Sp. gr. 4·545. Some grains of this mineral are strongly magnetic; some slightly, others not at all. (Klaproth.) Octohedrons.

g. The same. (H. Rose.)

h. *Menaccanite*, from Cornwall. Square prisms. (Chenevix.)

i. The same. (Klaproth.)

k. *Nigrine*, from Ohlapian. Sp. gr. 4·45. Not fusible before the blowpipe. Square prisms, of a reddish-black colour, translucent, and exhibiting a blood-red colour at the edges. (Klaproth.)

The octohedral varieties of titaniferous iron should perhaps be regarded as magnetic iron ore, Fe^3O^4, in which a portion of the iron is replaced by titanium. This view is supported by the following analysis, by Rammelsberg (*Pogg.* 53, 129), of the so-called magnetic iron-ore in the basalt of Uskel: for,

$$4FeO, 2Fe^2O^3, TiO^2 = 8Fe + Ti + 12O = 9 \text{ Metal} : 12 \text{ Oxygen} = 3 : 4.$$

The same formula probably belongs to the analyses *a*, *b*, *c*. in the preceding table, whereas iserine is probably $2FeO, TiO^2$, which would require it to contain 63·63 p. c. ferrous oxide and 36·36 titanic acid. (Gmelin.)

			Rammelsberg.
4FeO	140	41·67	39·16
$2Fe^2O^3$	156	46·43	48·07
TiO^2	40	11·90	11·51
	336	100·00	98·74

C. Titanate of Ferric Oxide, or Ferric Titanate.—When finely pounded titaniferous iron is very strongly ignited with several times its weight of chloride of calcium, and the fused mass freed, first from chloride of calcium and chloride of iron by digestion in water, and then from titanate of lime by strong hydrochloric acid, titanate of ferric oxide is left behind, in the form of long, thin, opaque, non-magnetic needles, having a dark steel-blue colour and strong lustre. They dissolve readily in red-hot melted bisulphate of potash, forming a yellow liquid, which, after solidification, dissolves perfectly in water. The crystals suffer no alteration by ignition in air or chlorine gas, or by boiling with oil of vitriol or strong hydrochloric acid. (Wöhler & Liebig, *Pogg.* 21, 578.)

D. Bifluoride of Titanium with Sesquifluoride of Iron.—The yellow aqueous mixture of the two salts yields, by spontaneous evaporation, a yellow syrup, and then, by evaporation at a gentle heat, a pale yellow, crystalline mass of salt, which is decomposed on being again dissolved in water. (Berzelius.)

Iron and Tantalum.

A. Tantalide of Iron.—Formed by igniting tantalic oxide with iron filings in a charcoal crucible. Imperfectly fused metal, resembling cast-iron, but not crystalline at the fracture. Scratches glass; brittle, but difficult to break in pieces; yields a dark brown powder. Hydrochloric acid slowly extracts the iron from it, leaving the tantalum in the form of a grey powder. (Gahn, Berzelius & Eggertz.)

B. Tantalite of Ferrous Oxide, or Ferrous Tantalite.—*Tantalite, yielding a cinnamon-coloured powder.* Of indeterminate crystalline form; sp. gr. 7·655. Scratches glass; exhibits an uneven, black, and copper-coloured fracture; opaque, black, and possessed of a higher metallic lustre than ordinary tantalite. Infusible before the blowpipe. With borax it forms a green glass, with white particles floating in it; but the solution is very slow, even when the mineral is pounded: the glass becomes milky on cooling. In microcosmic salt it dissolves easily, exhibiting the same colours as ordinary tantalite.

	Tantalite.				Berzelius. Kimito.
MnO	36	....	1·52	.....	1·61
9FeO	315	....	13·34	.....	12·93
$10TaO^2$	2010	....	85·14	.....	85·67
CaO		....		.....	0·56
SiO^2		....		.....	0·72
SnO^2		....		.....	0·80
	2361	....	100·00	.....	102·29

C. Tantalate of Ferrous Oxide, or Ferrous Tantalate.—*a. Bibasic.—Columbite.*—Crystalline system the right prismatic. Right rhombic prisms, with the lateral edges truncated, and numerous accumination faces. *Fig.* 74 (nearly) and other forms. $u' : u = 100°40'$; [illegible]=59°. Sp. gr. 5·9 to 6·46. Scratches glass. Fracture somewhat [illegible]oidal, and imperfectly laminar. Opaque, with metallic lustre, [illegible]-black, producing a dark brown powder. It is not magnetic, even [illegible]nition with charcoal. Before the blowpipe, it becomes somewhat

rounded at the corners; dissolves slowly in borax, to which it imparts a blackish-green colour; may be disintegrated by fusion with hydrate of potash. Fused with nitre, it forms a green mass, from which water extracts manganate and tantalate of potash.

	Columbite.			Wollaston. America.	A. Vogel.	Dunin-Borrowsky. Bodenmais.		Thomson.
1MnO	36	4·29		5	5	4·0		7·55
5FeO	175	20·89		15	17	20·0		14·00
$3TaO^3$	627	74·82		80	75	75·0		79·65
SnO^2					1	0·5		0·50
HO								0·05
	838	100·00		100	98	99·5		101·75

b. Monobasic.—Ordinary Tantalite.—Crystalline system the right prismatic. Right rhombic prisms, with truncated lateral edges, and acuminated with numerous faces, four of which belong to a rhombic octohedron. $u' : u = 122° 54'$; $i : i = 54° 4'$. Sp. gr. 7·264. (Nordenskiold, *Pogg.* 50, 656.) Fracture uneven, and exhibiting the metallic lustre. The mineral is black and opaque, and yields a black-brown powder, which becomes coffee-coloured when rubbed very fine. Infusible before the blowpipe. With carbonate of soda in the inner flame, it often yields globules of tin, especially if a little borax be added. With borax it fuses readily, forming a clear yellow glass, which becomes milk-white by flaming. In microcosmic salt it dissolves somewhat less readily, forming a brownish-yellow glass, which becomes yellow on cooling, and acquires a yellowish-red colour in the inner flame. Disintegrated by fusion with hydrate of potash. Dissolves in red-hot bisulphate of potash, forming a reddish-yellow liquid, solidifying, as it cools, in a white mass, which, when dissolved in water, leaves tantalic acid (together with stannic acid). Not attacked by acids, even strong oil of vitriol acting on it but slightly. (Gahn & Berzelius, *Schw.* 16, 259, 283 and 447.)

	At.	*Tantalite.*			Nordenskiold. Tamela.
MnO					1·12
FeO	1	35	14·34		13·75
TaO^3	1	209	85·66		83·44
SnO^2					trace
		244	100·00		98·31

	At.				Berzelius. Kimito.
MnO	1	36	7·36		7·4
FeO	1	35	7·16		7·2
TaO^3	2	418	85·48		83·2
SnO^2					0·6
		489	100·00		98·4

The following varieties of tantalite are mixed with considerable quantities of tin-stone, and partly also of wolfram: the sesquioxides of manganese and iron found in them should perhaps be estimated as protoxides.

	Berzelius.				
	Finbo.		Brodbo.		
CaO	2·40		1·19	to	1·50
Mn^2O^3	7·98		7·15	,,	6·61
Fe^2O^3	7·67		9·58	,,	11·08
TaO^3	66·99		68·22	,,	66·39
SnO^2	16·75		8·26	,,	8·41
WO^3			6·19	,,	6·13
	101·79		100·59	,,	100·12

Iron and Tungsten.

A. Tungstate of Ferrous Oxide, or Ferrous Tungstate.—*a. Monotungstate.*—Aqueous monotungstate of potash yields with neutral ferrous salts a light brown precipitate, which, when heated, gives off half its water and assumes a darker brown colour; is not decomposed by cold sulphuric, hydrochloric, or nitric acid, but completely at a boiling heat, with separation of tungstic acid; and dissolves in boiling phosphoric acid, likewise in warm oxalic acid, in which it forms a yellow solution, but is not soluble in water. (Anthon, *J. pr. Chem.* 9, 343.)

	Ignited.			Anthon.		*Hydrated.*			Anthon.
FeO	35		22·58	23·81	FeO	35		19·23	20
WO^3	120		77·42	76·19	WO^3	120		65·93	64
					3HO	27		14·84	16
	155		100·00	100·00		182		100·00	100

To this head likewise belongs *Wolfram*, in which, however, sometimes a larger, sometimes a smaller proportion of ferrous tungstate is replaced by manganous tungstate.—Crystalline system the right prismatic; right rectangular prisms, with the summits and lateral edges truncated. (Hauy.) According to Mohs, it belongs to the oblique prismatic system; $u' : u = 98° 12'$. Sp. gr. 7·1 and 7·6. Hardness between fluorspar and felspar. Opaque, with a metallic and adamantine lustre, and brownish-black colour; powder red-brown.—In a charcoal crucible heated in a blast-furnace, it is reduced, with loss of 40 to 46 per cent., to a perfectly united metallic mass. (Vauquelin.)—On charcoal before the blowpipe, it fuses with tolerable facility into an iron-black, magnetic globule, exhibiting externally an aggregation of laminar crystals. With carbonate of soda on charcoal, it is reduced to tungstide of iron, easily separated by levigation. Dissolves with tolerable facility in borax, exhibiting the iron reaction, and easily in microcosmic salt, forming in the outer flame a green, and in the inner a dark red glass, which is opaque even with a small quantity of wolfram, turns green if fused with tin for a short time, and reddish after a longer time.—Wolfram may be decomposed by fusion with hydrated carbonate or bisulphate of potash, likewise with chloride of calcium. When the decomposition is effected by hydrate or carbonate of potash, the products are tungstate of potash, which may be extracted by water, and a residue of oxidized iron and maganese; bisulphate of potash yields soluble salts of iron and manganese, and a residue of tungstic acid; chloride of calcium produces soluble chloride of iron and chloride of manganese, and insoluble tungstate of lime.—With hot oil of vitriol, wolfram forms an indigo-coloured solution, which loses its colour in the air, and deposits white flakes. (Schaffgotsch.)—Hot hydrochloric acid

digested with pounded wolfram, slowly extracts the oxides of iron and manganese, and leaves the tungstic acid in the form of a yellow powder. When pounded wolfram is digested with strong hydrochloric acid in close vessels, the acid dissolves, besides the iron and manganese, a small quantity of tungstic acid—which is precipitated on the addition of water—and leaves a swollen, dirty-blue powder, which turns yellow in the air, and gives up its protoxide of iron to hydrochloric acid, and its tungstic acid to ammonia, but not till the protoxide of iron has been converted into sesquioxide by exposure to the air. (Berzelius, *Schw.* 16, 478.) [For other observations relating to this subject, see below: Margueritte and Ebelmen.] The mineral is decomposed by strong aqua-regia more quickly than by hydrochloric acid; the small quantity of tungstic acid dissolved in the liquid, is precipitated together with iron on the addition of water. (Vauquelin, *Ann. Chim. Phys.* 30, 194.)

	At.			Count Schaffgotsch. *a.*	*b.*	Ebelmen. *c.*	Vauquelin. *d.*
MgO						0·80	
MnO	1	36	4·64	4·74	4·97	4·48	5·75
FeO	4	140	18·04	19·16	19·24	19·19	20·77
WO^3	5	600	77·32			76·20	
		776	100·00			100·67	

a. is Wolfram from Ehrenfriedersdorf;—*b.* from Monte Video, sp. gr. 7·544;—*c.* and *d.* from Limoges.

	At.			Berzelius. *e.*	Schaffgotsch. *f.*
MnO	1	36	5·80	5·76	6·05
FeO	3	105	16·91	17·97	17·95
WO^3	4	480	77·29		80·52
		621	100·00		104·52

	At.			Vauquelin. *g.*
MnO	2	72	9·27	10·86
FeO	3	105	13·51	13·08
WO^3	5	600	77·22	
		777	100·00	

e. is Wolfram from Cumberland;—*f.* from Chanteloupe, sp. gr. 7·437;—*g.* from the Département de la Haute Vienne. The sesquioxides of iron and manganese found by Vauquelin (*J. Chim. Méd.* 1, 244) are reckoned in the table as protoxides.

	At.	From Zinnwald.			Schaffgotsch.
CaO					0·48
MnO	3	108	13·88	13·28	13·96
FeO	2	70	9·00	9·52	9·62
WO^3	5	600	77·12		75·99
		778	100·00		100·05

Count Schaffgotsch (*Pogg.* 52, 475) regards wolfram, not as tungstate of ferrous oxide (and manganous oxide), but as a compound of tungstous oxide (IV. 25) with ferrous oxide (and manganous oxide) = $(FeO; MnO)WO^2$, because, if the tungstic acid obtained in the analysis be reckoned as such and not as tungstous oxide, the result is 4 or 5 per cent. in excess. This excess, however, does not occur in all analyses of wolfram; and, more-

over, no instance is known of tungstous oxide playing the part of an acid. Again, if the tungsten were in the state of tungstous oxide, no tungstic acid could be separated by the action of the hydrochloric acid out of contact of air. The observation of Wöhler & Beringer (*Ann. Pharm.* 39, 253), that wolfram heated in a stream of chlorine gas, yields, like tungstous oxide, a sublimate of tungstate of tungstic chloride (IV., 36), appears to be favourable to this theory of Schaffgotsch; Ebelmen, however, (*N. Ann. Chim. Phys.* 8. 405) endeavours to explain it by supposing that the ferrous oxide and tungstic acid decompose each other, yielding ferric oxide and tungstous oxide; but this hypothesis is inadmissible, excepting when the residue contains a basic sulphate of ferric oxide and manganous oxide.

On the other hand, Margueritte (*Compt. rend.* 17, 742) regards wolfram as a compound of ferric and manganic oxide with tungstic oxide = Fe^2O^3,W^3O^9 mixed with Mn^2O^3,W^3O^9. In support of this view, the following facts are adduced:—When pounded wolfram is digested in a close vessel with hydrochloric acid not very hot, ferric oxide is dissolved and blue oxide of tungsten left behind; but if the solution be boiled, or left for some time in contact with the residue, hydrochlorate of ferrous oxide and yellow tungstic acid are formed.—Ebelmen, on the contrary (*Compt. rend.* 17, 1198), by placing fine wolfram powder in contact with cold strong hydrochloric acid out of contact of air, obtained a liquid, which, on the addition of water, deposited tungstic acid, and retained in solution protoxide of iron free from sesquioxide; it was only when the quantity of ferrous hydrochlorate was increased by the continued action of the hydrochloric acid, that the separated tungstic acid was mixed with blue particles. Tungstic acid (precipitated from tungstate of ammonia by hydrochloric acid), when digested with hydrochlorate of ferrous oxide and strong hydrochloric acid, is immediately converted—with simultaneous formation of a small quantity of ferric hydrochlorate—into blue oxide of tungsten free from iron, which again becomes yellow on the addition of water, and consequently is not produced at all when dilute hydrochloric acid is employed. Hence, when wolfram is decomposed by concentrated hydrochloric acid, part of the separated tungstic acid is reduced to the state of tungstic oxide by the action of the ferrous hydrochlorate produced.

b. Bitungstate.—Formed by precipitating a ferrous salt with an alkaline bitungstate. The cinnamon-coloured, curdy precipitate hardens even under the liquid, and dries up to a mass of rusty-brown powder, which bakes together when ignited, and at the same time gives off water and assumes a darker colour. Insoluble in water, but soluble in hot aqueous phosphoric and oxalic acid. (Anthon.)—By precipitating a ferrous salt with a hot saturated solution of bitungstate of ammonia, a brick-red precipitate is obtained. Dilute hydrochloric acid extracts protoxide of iron from it, leaving the tungstic acid; strong hydrochloric acid extracts sesquioxide of iron as well as protoxide, and imparts a blue colour to the separated tungstic acid; cold potash-ley dissolves out the tungstic acid, and leaves greenish-white hydrate of ferrous oxide. (Ebelmen, *Compt. rend.* 17, 1198.)

	Ignited.		Anthon.		*Dried in the air.*		Anthon.
FeO	35	12·73	12·77	FeO	35	11·94	12
$2WO^3$	240	87·27	87·23	$2WO^3$	240	81·91	82
				2HO	18	6·15	6
	275	100·00	100·00		293	100·00	100

B. Carbide of Tungsten and Iron.—Tungstic acid, heated in the forge-fire with cast-iron, yields a brownish-white, hard, granular compound. (De Luyart.)

C. Ferrous Sulphotungstate.—FeS,WS^3.—Ferrous sulphate forms a deep yellow solution with sulphotungstate of potassium.

D. Ferric Sulphotungstate.—$Fe^2S^3,3WS^3$.—Aqueous sulphotungstate of potassium yields, with ferric salts, a dark brown, bulky precipitate, which dries up to a liver-coloured mass. (Berzelius.)

Iron and Molybdenum.

A. Molybdide of Iron.—Bluish-grey, hard, brittle, fine-grained, magnetic; fusible before the blowpipe, when formed of equal parts of the two metals, but not when formed of 2 pts. molybdenum and 1 pt. iron.

Many samples of pig-iron likewise consist of iron alloyed chiefly with molybdenum; *a*. Pig-iron from the upper works at Eisleben, obtained in the fusion of bituminous marl-slate in smelting-furnaces.—*a*. Fine-grained. —*β*. Coarse-grained. (Heine, *J. pr. Chem.* 9, 176.)—*b*. The so-called Magdeburg meteoric iron, containing slag mixed with bronze-yellow copper-cinder; probably the pig of iron from a copper-furnace.—*α*. is the analysis of a fine-grained sample, *β*. of a coarse-grained sample, by Stromeyer (*Pogg.* 28, 551);—*γ*. is the analysis by Wehrle. (*Zeitschr. Phys. v. W.* 3, 168.)—Pig of iron found in the neighbourhood of the *rothe Hütte* in the Harz, examined by Wiggens. (*Pogg.* 28, 565.)—*d*. Pig of iron found underground at Lauchstadt. (Steinberg, *J. pr. Chem.* 18, 379.)

	a, *α*.	*a*, *β*.	*b*, *α*.	*b*, *β*.	*b*, *γ*.	*c*.	*d*.
Ca						0·29	trace
MgO,Al^2O^3							trace
Mn			0·01	0·02	0·12	0·14	
Fe	57·91	73·26	74·60	76·77	73·11	81·14	50 to 80
Co	0·67	0·77	3·07	3·25	4·16	2·40	trace
Ni	3·42	4·63	1·28	1·15	0·84	trace	1 to 6
Cu	2·45	1·79	4·32	3·40	5·34	7·69	2 to 4
Ag					trace		
Mo	28·49	9·13	10·19	9·97	5·28	1·08	10 to 30
Si			0·39	0·35	1·83	1·94	
C	0·87	1·42	0·48	0·38	1·20	0·69	trace
As			2·47	1·40	2·70	1·82	
P	3·52	6·05	2·27	1·25	1·38	0·81	2 to 5
S	0·60	0·09	0·92	2·06	2·94	0·62	trace
	97·93	97·14	100·00	100·00	98·90	98·62	

B. Molybdate of Ferric Oxide, or Ferric Molybdate.—Hydrochlorate of ferric oxide gives a brown precipitate with molybdate of potash. (Scheele.)

C. Ferrous Sulphomolybdate.—FeS,MoS^3.—Formed in the preparation (1) of sulphomolybdate of potassium, its formation being due to the iron contained in the native sulphide of molybdenum. (IV. 57.) When the greater part of the sulphomolybdate of potassium has been removed from the ignited mass by water, the iron-compound likewise dissolves and imparts a deep wine-red colour to the liquid. On evaporating this solution, the iron-compound is precipitated in the form of a black

chromic acid to 25·06 ferric oxide, is not rendered turbid either by dilution with water or by boiling, and yields, on evaporation, a brown resinous mass, soluble in water and alcohol. (Maus, *Pogg.* 9, 132.)

D. Carbide of Chromium and Iron.—*a. Comparatively rich in Chromium.*—1. A mixture of chromic and ferric oxide is exposed to a very intense heat in a charcoal crucible.—2. One hundred parts of chrome-iron-ore are fused in a charcoal crucible, with 70 silica and 30 lime, or with 100 parts of glass, or with 40 of borax. These fluxes take up the earths mixed with the chrome-iron-ore, and form a slag; the purer the ore, the less flux does it require; the addition of 60 parts of ferric oxide increases the quantity of chrome-iron in the product.—Hard, brittle, crystalline, whiter than iron and highly lustrous; less fusible, less magnetic, less easily attacked by acids than iron; all these properties are exhibited in a higher degree, the larger the proportion of the chromium. The compound obtained by (1) from equal parts of chromic and ferric oxides, exhibits a crystalline fracture—contains hollows filled with prismatic crystals—scratches glass as strongly as diamond—is whiter than platinum—and may be ground in an agate mortar to a fine powder, which exhibits the metallic lustre; it is but slightly attacked by acids, even by boiling aqua-regia, but may be oxidized by fusion with nitre. (Berthier, *Ann. Chim. Phys.* 17, 55; also *Schw.* 43, 419; also *Gilb.* 72, 247.)

b. Chrome-steel.—1. The alloy *a.* when fused with cast-steel, yields a very hard kind of steel, which is easy to work, and when treated with sulphuric acid, exhibits beautiful Damascus figures with silver-white veins. (Berthier.)—2. Three parts of chromium fused with 100 parts of steel, yield a very hard alloy, which, however, is not malleable at high temperatures as iron. By treating the polished surface with sulphuric acid, or by merely heating the alloy, beautiful Damascus figures are formed upon it. —3. The alloy of 1 pt. chromium and 100 steel, exhibits similar properties, but is somewhat softer. (Faraday & Stoddart.)

Iron and Uranium.

Uranide of Iron ?—When a mixture of an iron-salt with a uranium-salt is precipitated by ammonia, and the precipitated mixed oxides reduced by hydrogen gas at a red heat, the residue [compound or mixture ?] burns very vividly when thrown out into the air after cooling. (Arfvedson.)

Iron and Manganese.

A. Manganide of Iron.—Iron by combining with manganese, becomes whiter and more brittle; when the proportion of manganese amounts to 22 per cent., the iron ceases to exhibit magnetic properties. (Mushet.)

Hypermanganate of potash exhibits no alteration when mixed with hydrochlorate of ferric oxide. (Fromherz.)

¶ B. Manganiferous Magnetic Iron-ore.—*Iron-earth, Eisenmulm.* —(FeO; MnO) Fe^2O^3.—Occurs at the "Alte Borke" mine in the neighbourhood of Siegen, where a vein of spathic iron is broken through by basalt, and partly converted into magnetic iron-ore.—Black, pulverulent

mass, which attaches itself closely to anything on which it is rubbed, and is strongly attracted by the magnet. The specific gravity was found by experiment to be 3·76; but this is too low. It may be considered as magnetic iron-ore in which about half the ferrous oxide is replaced by manganous oxide, which is isomorphous with it. The analysis of three specimens gave the following results:

	(1.)		(2.)		(3.)
Fe^2O^3	66·71	.....		.....	65·68
FeO		.....	13·65	.....	14·09
MnO	17·11	.....	17·62	.....	16·25
CoO				.....	trace
CuO	traces	.....	traces	.....	0·09
CO^2				.....	trace
Water				.....	trace
Sand, &c.	1·34	.....	1·57	.....	2·34
					98·45

The specimens (2) and (3) contained small quantities of gold. (Genth. *Ann. Pharm.* 66, 277.) ¶

C. Carbide of Manganese and Iron.—Manganese unites readily with steel. The compound possesses great malleability at high temperatures, but is very brittle when cold. It exhibits very plain and perfectly black Damascus figures. (Bréant.)

D. Phosphate of Manganous Oxide and Ferrous Oxide.—*Manganoso-ferrous Phosphate.—a. Quadrobasic.—Triplite, Phosphormangan.*—Massive, having a flat conchoidal fracture, and specific gravity = 3·43. Harder than fluorspar; translucent at the edges; exhibits a faint waxy lustre; colour varying from pitch-black to clove-brown; powder yellowish-grey.—When heated, it gives off a small quantity of water containing hydrofluoric acid. Fuses readily on charcoal before the blowpipe, effervescing strongly, and yielding a black, metallic-shining, strongly-magnetic bead, which, when heated with carbonate of soda in the inner flame, yields a large quantity of phosphide of iron. With carbonate of soda on platinum, it yields mineral chameleon. Dissolves easily in borax, exhibiting the reaction of manganese in the outer, and of iron in the inner flame.—In microcosmic salt it dissolves still more readily, scarcely exhibiting the latter reaction, and requiring very long-continued and gradual treatment in the outer flame to make it exhibit the reaction of manganese. Easily soluble in hydrochloric acid. (Berzelius.)

	Triplite.				Berzelius. Limoges.
4MnO	144·0	....	33·74	....	32·60
4FeO	140·0	....	32·80	....	31·90
$2PO^5$	142·8	....	33·46	.....	32·78
$3CaO,PO^5$		....		.....	3·20
$4MnO,PO^5+4FeO,PO^5$	426·8	....	100·00	.....	100·48

The triplite of Limoges, when heated with oil of vitriol, etches glass so strongly, that it might be supposed to be allied to iron-apatite. (Gmelin.)

b. Terbasic.—a. Triphyline.—$3(LiO; MnO; FeO)PO^5$, or more exactly: $3(\frac{3}{15}LiO, \frac{1}{15}MnO, \frac{12}{15}FeO)PO^5$. Crystalline system the oblique prismatic. The cleavage-planes indicate a form like *Fig.* 85, without *f*- and *a*-faces, $u' : u = 132°$ nearly. Cleavage distinct parallel to i; less distinct parallel

to *u* and *t*. Sp. gr. 3·6; hardness less than that of apatite. Slightly translucent, with a tolerably strong waxy lustre; greenish-grey, bluish in places; powder greyish-white. Gives off a small quantity of water when heated. Decrepitates before the blowpipe, and then fuses very easily and quietly to a dark steel-grey, magnetic bead, at the same time imparting to the flame a pale bluish-green colour, reddish at intervals, and after moistening with sulphuric acid, a deeper blue-green. When fused on platinum with carbonate of soda, it exhibits a slight manganese reaction; in borax it dissolves with the reaction of iron. Gives up phosphoric acid to caustic potash. Easily soluble in hydrochloric acid; the solution evaporated to dryness and boiled with alcohol, imparts a purple-red colour to the flame of the alcohol. (Fuchs, *J. pr. Chem.* 3, 98; 5, 319.)

	Triphyline.				Fuchs. Rabenstein.		Fuchs. Or.
2LiO	28·8	....	3·42	.....	3.40	....	3·45
MnO	36·0	....	4·28	.....	4·70	....	4·75
12FeO	420·0	....	49·89	.....	48·57	....	49·16
$5PO^5$	357·0	....	42·41	.....	41·47	....	42·64
SiO^2		....		.....	0·53		
HO		....		.....	0·68		
	841·8	....	100·00	.....	99·35	....	100·00

β. *Tetraphyline* or *Perowskine*.—3(LiO; MgO; MnO; FeO),PO^5, or more exactly: $3(\frac{7}{24}LiO,\frac{1}{24}MgO,\frac{4}{24}MnO,\frac{12}{24}FeO)PO^5$.—From Keiti near Tamela.—Resembles triphyline in its outward aspect, but its fracture is yellow when fresh, and gradually blackens by exposure to the air. It likewise gives a stronger manganese-reaction before the blowpipe. With carbonate of soda on platinum, it colours the blowpipe-flame red. With boracic acid and iron wire, it yields phosphide of iron. (Berzelius & Nordenskiold, *Pogg.* 36, 473.)

	Tetraphyline.				Berzelius & Nordenskiold.
7LiO	100·8	.....	8·03	.....	8·2
MgO	20·0	.....	1·59	.....	1·7
4MnO	144·0	.....	11·47	.....	12·1
12FeO	420·0	.....	33·43	.....	38·6
$8PO^5$	571·2	.....	45·48	.....	42·6
	1256·0	.....	100·00	.....	103·2

γ. *Iron-apatite*.—$3[3(MnO; FeO)PO^5]+FeF$, or more fully: $3MnO, PO^5+2(3FeO,PO^5)FeF$.—The cleavage-planes of the imperfectly crystallized mass appear to correspond to a six-sided prism. Sp. gr. 3·97. Hardness equal to that of apatite. Has a waxy lustre, and clove-brown colour. Decrepitates before the blowpipe and fuses readily, with intumescence, into a metallic-shining, bluish-black, strongly-magnetic globule. Dissolves easily in borax and in microcosmic salt. With heated oil of vitriol, it gives off hydrofluoric acid. Warm hydrochloric acid dissolves it with facility. (Fuchs, *J. pr. Chem.* 18, 499.)

	Iron-apatite.				Fuchs. Zwiesel.
3MnO	108·0	.....	18·70	.....	20·34
6FeO	210·0	.....	36·35	.....	35·44
$3PO^5$	214·0	.....	37·04	.....	35·60
Fe	27·0	.....	4·67	.....	4·76
F	18·7	.....	3·24	.....	3·18
Quartz		.....		.....	0·68
	577·7	.....	100·00	.....	100·00

c. 5 atoms of Base to 2 atoms of Acid.—α. Hetepozite.—5(MnO; FeO), $2PO^5+2$ Aq.? [Does it not likewise contain lithia?]—Laminated mass, having three planes of cleavage, which indicate a rhombic prism whose lateral dihedral angles are about 100° and 80°. Sp. gr. of the unaltered mineral 3·524; of the same altered by weathering, 3·390. Scratches glass but not quartz. Has a faint waxy lustre, and a greenish-grey colour inclining to bluish-grey; the faces which are exposed to the air exhibit a semi-metallic lustre and violet colour. Before the blowpipe it fuses into a dark brown globule, having a semi-metallic lustre. Dissolves in hydrochloric acid with the exception of a small quantity of silica. (Dufrénoy, *Ann. Chim. Phys.* 41, 337; abstr. *Pogg.* 17, 495.) In its primitive state the mineral yields, sometimes a grey, sometimes a yellow powder; after weathering, it yields a violet powder. With hydrochloric acid it evolves chlorine, and must therefore contain free manganic oxide. (Vauquelin, *Ann. Chim. Phys.* 30, 294.)

	Hetepozite.				Dufrénoy.		Vauquelin.
5MnO	180·0	....	17·78	.....	17·57	....	16·5
10FeO	350·0	....	34·57	.....	34·89	Fe^2O^3	33·5
$6PO^5$	428·4	....	42·32	.....	41·77	....	50·0
6HO	54·0	....	5·33	.....	4·40	....	5·0
SiO^2		....		.....	0·22	....	2·5
	1012·4	....	100·00	.....	98·85	....	107·5

β. Huraulite.—5(MnO; FeO), $2PO^5+8$Aq?—Crystalline system the right prismatic, *Fig.* 99, sometimes with the *t*-face. $u : u'=62° 30'$; $\alpha : \alpha=80°$. No cleavage-planes. Fracture conchoidal. Sp. gr. 2·270. Harder than calcspar, transparent, and of a hyacinth-red colour. Gives off water when heated, and fuses very easily before the blowpipe to a black globule, having a semi-metallic lustre. (Dufrénoy, *Ann. Chim. Phys.* 41, 337; abstr. *Pogg.* 17, 493.)—White with a tinge of rose-colour. (Vauquelin; *Ann. Chim. Phys.* 30, 294.)

	Huraulite.				Dufrénoy.		Vauquelin.
15MnO	540·0	....	34·30	.....	32·85	....	} 47·2
5FeO	175·0	....	11·12	.....	11·10	Fe^2O^3	
$8PO^5$	571·2	....	36·29	.....	38·00	....	32·8
32HO	288·0	....	18·29	.....	18·00	....	20·0
	1574·2	....	100·00	.....	99·95	....	100·0

E. Phosphate of Ferric Oxide and Manganic Oxide, or Manganico-ferric Phosphate.—*Weathered Triphyline* or the so-called *Triplit of Bodenmais.*—$6(Mn^2O^3; Fe^2O^3)\ 4PO^5+5Aq$.

					Fuchs.
$1Mn^2O^3$	80·0	....	10·00	.....	8·94
$5Fe^2O^3$	390·0	....	48·71	.....	48·17
$4PO^5$	285·6	....	35·67	.....	35·70
5HO	45·0	....	5·62	.....	5·30
SiO^2		....		.....	1·40
	800·6	....	100·00	.....	99·51

Iron and Arsenic.

A. Arsenide of Iron.—*a. Di-arsenide.*—54 pts. (2 At.) of iron filings ignited in a close vessel with 108 pts. of arsenic, retain 73·44 (nearly 1 At.) arsenic in combination. (Gehlen.) The arsenide of iron

thus formed does not fuse; it is white, very brittle, and easily pulverized. (Bergman, Gehlen.)

b. Found in the form of *Arsenical Iron* or *Arsenical Pyrites.*—Crystalline system the right prismatic. Form, a right rhombic prism: $u:u'=122° 26'$; bevelled with two *y*-faces resting on the two obtuse angles. Cleavage parallel to *p*. Sp. gr. 7·22. Hardness intermediate between fluorspar and felspar. Silver-white inclining to steel-grey; powder blackish-grey. (Mohs.) When heated in closed vessels, it yields a sublimate of arsenic; fuses on charcoal before the blowpipe to a black magnetic mass, at the same time emitting a strong odour of arsenic. Dissolves in nitric acid with separation of arsenious acid.

	At.			E. Hofmann.		Th. Scheerer.		Hofmann.
				a, α.	*b, α.*	*b, β.*	*b, β.*	*c.*
Fe	1	27	26·47	28·06	28·76	28·14	27·87	13·49
Co								5·10
Ni								13·37
As	1	75	73·53	65·99	71·24	70·22	72·13	60·41
S				1·94		1·28		5·20
Serpentine				2·17				
	1	102	100·00	98·16	100·00	99·64	100·00	97·57

a. is arsenical pyrites from Reichenstein,—*b.* from Fossam,—*c.* from Sladmig; in this last, the iron is partly replaced by cobalt and nickel.—*a, α.* and *b, α.* are the direct results of analysis; if from these we deduct the matrix and sulphur, together with the quantity of iron and arsenic required to convert the sulphur into arsenical pyrites, the iron and arsenic will remain in the proportions calculated in *a, β.* and *b, β.* (*Comp.* E. Hofmann and Th. Scheerer, *Pogg.* 25, 489; 49, 536; 50, 153.)

B. Arsenite of Ferrous Oxide, or Ferrous Arsenite.—Arsenite of ammonia forms with green vitriol a greenish-white precipitate which afterwards becomes yellowish; it dissolves in aqueous ammonia forming a greenish-yellow solution, but not in arsenite of ammonia or other ammoniacal salts. (Wittstein.)

When hydrated ferrous oxide precipitated by ammonia and washed (it then contains 3 parts of the anhydrous oxide) is agitated with an aqueous solution of 1 pt. arsenious acid, it is partially dissolved. The filtrate [which Guibourt regards as ferrous arsenite] evolves a large quantity of arsenic in Marsh's apparatus, and gives with sulphuretted hydrogen a brown colouring, which disappears on the addition of hydrochloric acid, without the formation of a yellow precipitate [was there not at least a precipitate of sulphur arising from the reduction of the sesquioxide of iron to protoxide?]—The solution is also coloured yellow by ammonia, deep yellow by cupro-sulphate of ammonia, and instantly black by tincture of galls. (Guibourt.)

C. Arsenite of Ferric Oxide, or Ferric Arsenite.—*Quadrobasic.*—Formed when acetate of ferric oxide is precipitated by free arsenious acid or an alkaline arsenite. The free acid precipitates the ferric oxide completely from a solution of the acetate, but not at all from the sulphate, hydrochlorate, or nitrate. (Bunsen.) The precipitate formed by arseniate of ammonia in a solution of ferric acetate requires long-continued washing to free it from acetate of ammonia. (Simon.)—2. The same salt *is produced* by agitating freshly-precipitated ferric hydrate with aqueous

arsenious acid. 1 part of arsenious acid dissolved in water is completely precipitated by a quantity of ferric hydrate containing from 10 to 12 parts of the dry oxide; the precipitation is almost complete even with a smaller quantity of the hydrate. (Bunsen.) To precipitate 1 part of arsenious acid from its aqueous solution, 6·67 parts of dry ferric oxide in the hydrated state are not quite sufficient, and 10 pts. are more than sufficient. (Guibourt.)

The precipitate obtained by the first method is bulky, yellowish-brown, resembles hydrated ferric oxide in appearance, and dries up to a pitch-black mass, which has a conchoidal, waxy fracture, and yields an ochre-yellow powder. (Bunsen.)—When heated in a glass tube, it gives off water and arsenious acid, but a portion of acid always remains behind in combination with the oxide. (Bunsen.) The salt obtained by method (2) leaves, when ignited, 67 per cent. of ferric oxide still containing arsenic. (Guibourt.) The residual ferric oxide is free from arsenic. (Simon, *Pogg.* 40, 442.)—The stronger acids dissolve the salt, with separation of arsenious acid. Acetic acid has no action on the salt, even when recently precipitated. (Bunsen; *vid.* Bunsen and Berthold: *das Eisenoxydhydrat u. s. w.* Gött. 1834.)

					Bunsen.
Fe^2O^3	312	....	68·42	.....	68·28
AsO^3	99	....	21·71	.....	21·73
5HO	45	....	9·87	.....	9·99
$4Fe^2O^3,AsO^5+5Aq.$	456	....	100·00	.....	100·00

b. Sesqui-arsenite?—When green vitriol oxidized by aqua-regia and then neutralized with ammonia, is mixed with a saturated solution of arsenious acid in hot soda-ley, freed from the excess of arsenious acid by cooling, there is produced, after 12 hours, an abundant yellow precipitate, which increases, if the supernatant liquid, as it becomes acid, is again neutralized with ammonia till it completely loses its colour.—Deep yellow while moist, but after drying it becomes ruby-red, transparent, hard, and yields a yellow powder. The salt, after being dried in the air, loses 11·6 per cent. of water at 100°. A hundred parts of the salt dried at 100°, give off at a red heat the greater part of the arsenious acid, together with a small quantity of water, and leave 38·82 parts of ferric oxide, still containing arsenious acid; by longer ignition, this quantity is reduced to 34·16 parts, but even then the residue is not quite free from arsenic. Hence the anhydrous salt must be regarded as $2Fe^2O^3,3AsO^3$, and the salt dried in the air, as $2Fe^2O^3,3AsO^3+7Aq$. The salt gives with caustic soda a deep red solution which is not rendered turbid by carbonic acid, and when evaporated leaves a reddish residue, perfectly soluble in water. (Guibourt, *J. Chim. Méd.* 15, 306; also *N. Br. Arch.* 23, 69.)

D. Arseniate of Ferrous Oxide, or Ferrous Arseniate.—*a. Terbasic.*—Arseniate of ammonia forms a white precipitate with sulphate of ferrous oxide. (Chenevix.)

					Chenevix.
3FeO	105	....	38·32	.....	43
AsO^5	115	....	41·97	.....	38
6HO	54	....	19·71	.....	19
	274	....	100·00	.....	100

b. Bibasic.—The white precipitate which ferrous salts form with arseniate of ammonia—the composition of which, whether bibasic or

terbasic, has not yet been determined—assumes a dingy green colour on exposure to the air. When heated, it evolves arsenious acid and leaves a grey residue containing ferric oxide. It dissolves sparingly in ammonia, forming a liquid which turns green in the air. (Berzelius.) The ammoniacal solution is greenish-yellow, and does not become turbid on exposure to the air, even for several hours; the salt does not dissolve in arseniate of ammonia or in other ammoniacal salts. (Wittstein.)

c. Acid Salt.—Iron dissolves in aqueous arsenic acid. (Scheele.) If the acid acts for several weeks without contact of air, [mono ?] arseniate of ferrous oxide is deposited in asbestus-like threads united in spherical masses, together with black needles of metallic arsenic. (Fischer, *Pogg.* 9, 262.)

E. Ferroso-ferric Arseniate.—*a. Cube-ore.*—Belongs to the regular system, *Fig.* 1, 4, 5, 8. Cleavage parallel to the faces of the cube. Harder than calcspar. Translucent, with a glassy lustre, and pistachio-green colour, inclining to brownish-green; powder straw-yellow.—Gives off water and turns red when heated; swells up slightly on the application of a stronger heat, little or no arsenious acid subliming, and retains its red colour. When fused upon charcoal, it gives off a strong odour of arsenic, and fuses into a metallic-grey magnetic slag, which dissolves in borax or microscopic salt, emitting an arsenical odour and exhibiting the reaction of iron. (Berzelius.) Caustic potash extracts arsenic acid from it, and separates black, anhydrous ferroso-ferric oxide. Dissolves readily in hydrochloric or nitric acid, but not in water.

	At.	*Cube-ore.*		Berzelius. Cornwall.
CuO				0·60 to 0·65
FeO	1	35	12·41	
Fe^2O^3	1	78	27·66	40·56 „ 39·20
AsO^5	1	115	40·78	38·00 „ 37·82
PO^5				0·70 „ 2·53
HO	6	54	19·15	19·57 „ 18·61
Matrix				0·35 „ 1·76
$FeO,Fe^2O^3,AsO^5+6Aq.$		282	100·00	99·78 „ 100·57

Berzelius (*Ann. Chim. Phys.* 31, 413; *Jahresber.* 4, 144; 5, 206) supposes that part of the sesquioxide of iron found in the analysis is contained in the cube-ore in the form of protoxide; he gives as the formula of the mineral: $3FeO,AsO^5+3Fe^2O^3,2AsO^5+18Aq.$, which leads to the same composition per cent.

b. Skorodite.—Crystalline system the right prismatic. Right rhombic and rectangular prisms, accuminated with the faces of a rhombic octohedron. $u^l : u = 111° 34'$. Sp. gr. 3·16. Harder than calcspar. Translucent, appearing pale blue by transmitted light; has a vitreous lustre, and a leek-green colour inclining to brown; powder greenish-white. When heated, it first gives off water and assumes a greyish-white or yellowish colour; then, on the application of a stronger heat, it turns black and yields a sublimate of arsenious acid. Before the blowpipe, it behaves like cube-ore. (Berzelius.) When heated out of contact of air, it does not evolve arsenious acid, unless arsenical pyrites is mixed with it. (G. Rose.) Gives up arsenic acid to caustic potash; dissolves readily in hydrochloric acid.

	Skorodite.				Berzelius. Brazil.		Boussingault. Popayan.
$2FeO$	70	....	10·31	.....		....	
$2Fe^2O^3$	156	....	22·98	.....	34·85	...	34·3
$3AsO^5$	345	....	50·81	.....	50·78	...	49·6
$12HO$	108	....	15·90	.....	15·55	...	16·9
PO^5		....		.....	0·67	PbO	0·4
CuO		....			trace		
	679	....	100·00	.....	101·85	...	101·2

Boussingault (*Ann. Chim. Phys.* 41, 75) estimates all the iron in Skorodite as sesquioxide; Berzelius reckons part of it as protoxide, according to the formula adopted in the calculation just given: $2FeO,AsO^5 + 2(Fe^2O^3,AsO^5) + 12Aq$.

F. Arseniate of Ferric Oxide, or Ferric Arseniate.—*a. Sixteen-basic.*—Formed by boiling *b* or *c* with excess of caustic potash. Brown like hydrated ferric oxide. When heated to commencing redness, it exhibits a peculiarly vivid incandescence. Does not give up any acid to caustic potash. Insoluble in ammonia.

					Berzelius.
$16Fe^2O^3$	1248	....	79·04	.....	79·6
AsO^5	115	....	7·28	.....	7·0
$24HO$	216	....	13·68	.....	13·4
$16Fe^2O^3,AsO^5 + 24Aq.$	1579	....	100·00	.....	100·0

b. Bibasic.—By oxidating bibasic ferrous arseniate with boiling nitric acid, and evaporating or precipitating with ammonia. Insoluble in ammonia. (Berzelius.)

White Iron-cinder from the *Fürstenstollen*, near Freiberg. Kidney-shaped, soft, knobby lumps, almost friable, and of a light yellow-grey colour; they have a coarse earthy fracture, and adhere somewhat strongly to the tongue. (Freiesleben.) This substance, when heated rather strongly, gives off a large quantity of water, containing a trace of sulphuric acid, at the same time shrinking together, and assuming a brownish-yellow colour. Continued ignition causes it to cake together into a black-brown slag. (Kersten, *Schw.* 53, 176.)

					Kersten.
$2Fe^2O^3$	156	....	41·16	.....	40·45
AsO^5	115	....	30·34	.....	30·25
$12HO$	108	..	28·50	.....	28·50
$2Fe^2O^3,AsO^5 + 12Aq.$	379	....	100·00	.....	99·20

c. Sesqui-arseniate.—Tersulphate of ferric oxide yields a white precipitate with diarseniate of soda:

$$2Fe^2Cl^3 + 3(2NaO, AsO^5) = 2Fe^2O^3,3AsO^5 + 6NaCl.$$

According to Pfaff, the same precipitate is produced by mono-arseniate of potash. When heated, it gives off its water and turns red, and at a low red heat exhibits a feeble glow; after cooling, it appears more yellowish than it originally was. (Berzelius.)

		Anhydrous.	
$2Fe^2O^3$	156	.....	31·15
$3AsO^5$	345	.....	68·85
$2Fe^2O^3,3AsO^5$	501	.....	100·00

	Hydrated.				Berzelius.		Chenevix.
$2Fe^2O^3$	156	....	25·62	.....	83·32	.....	37·2
$3AsO^5$	345	....	56·65				42·4
12HO	108	....	17·73	.....	16·68	.....	20·4
+12Aq.	609	....	100·00	.....	100·00	.....	100·0

Dissolves in hydrochloric and in nitric acid, and separates again on evaporation in the form of a white powder. Aqueous ammonia dissolves it immediately when recently precipitated, slowly after drying; according to Döbereiner (*Schw.* 26, 271) and Wittstein (*Repert.* 63, 329), the solution is yellow; but according to Berzelius (*Schw.* 32, 162), it is red. The ammoniacal solution, if it likewise contains sulphuric acid, deposits, after a few days, a reddish-yellow powder soluble in water. When evaporated, it leaves basic arseniate of ferric oxide and ammonia in the form of a ruby-coloured, transparent mass, full of cracks, having the appearance of an extract, and no longer smelling of ammonia. This mass, when subjected to dry distillation, gives off a large quantity of ammonia with water, then water, nitrogen gas, and a sublimate of arsenious acid, and leaves greyish-green ferroso-ferric arseniate. It is soluble in water containing ammonia, but is decomposed by pure water, which dissolves arseniate of ammonia, together with a quantity of undecomposed basic arseniate of ferric oxide and ammonia, and leaves diarseniate of ferric oxide undissolved. (Berzelius.) The ammoniacal solution remains clear when treated with ferrocyanide of potassium, not giving a precipitate of prussian blue till an acid is added. (H. Rose.) The salt is insoluble in water and acetic acid, and, according to Wittstein, in arseniate of ammonia and other ammoniacal salts.

G. Arsenio-sulphate of Ferric Oxide.—*Pittizite*, or *Brown Iron-cinder*.—Stalactitic. Sp. gr. 2·3 to 2·4. Harder than gypsum. Fracture conchoidal. Translucent, with a waxy lustre and brown colour; powder pale yellow. Gives off a large quantity of water when heated. At an incipient red heat, it evolves a considerable quantity of sulphurous acid, but yields no sublimate. When heated on charcoal, it shrinks together, evolving a strong arsenical fume. (Berzelius.) When gradually heated, it first gives of pure water, assuming a yellow colour and losing its transparency; then evolves sulphuric acid, mixed at a still later stage with sulphurous acid, and assumes a dark red-brown colour. At an incipient red-heat, it swells up and fuses into a porous, dark red-brown slag, which becomes blackish after longer ignition. When repeatedly boiled with water, it gives up to that liquid the whole of its sulphuric acid, free from ferric oxide and arsenic acid. Dissolves with facility in warm hydrochloric acid, less easily in nitric acid. (Stromeyer, *Untersuchung der Mineralkörper*, 244.) Loses 20 per cent. at a low red-heat, 45 at a higher temperature; dissolves with equal facility in hydrochloric and in nitric acid. (Laugier, *Ann. Chim. Phys.* 30, 325.)

					Stromeyer.		Laugier.
Mn^2O^3		....		.....	0·64	....	trace
$6Fe^2O^3$	468	....	33·96	.....	33·10	....	35
$3AsO^5$	345	....	25·04	.....	26·06	....	20
$4SO^3$	160	....	11·61	.....	10·04	....	14
45HO	405	....	29·39	.....	29·26	....	30
	1378	....	100·00	.....	99·10	....	99

$4(Fe^2O^3,SO^3)+2Fe^2O^3,AsO+45Aq$?—If the sulphuric acid, together with a certain quantity of water, can be regarded as an accidental admixture, the formula will be : $2Fe^2O^3,AsO^5+12Aq$.

H. Arseniate of Ferric Oxide and Lime.—*Ferrico-calcic Arseniate.*—*Arseniosiderite* from Romanèche. Fibrous ; sp. gr. 3·52 ; crumbles between the fingers. Colour brownish-yellow, becoming darker by exposure to the air. Fuses very easily before the blowpipe. Contains: KO 0·76—CuO 8·43—Fe^2O^3 41·31—Mn^2O^3 1·29—AsO^5 34·25—SiO^2 4·04—HO 8·75 (loss, 1·16). (Dufrénoy, *N. Ann. Chim. Phys.* 7, 382 ; also *J. pr. Chem.* 28, 315.) The analysis does not lead to any satisfactory formula.

I. Ferrous Sulpharsenite.—The solution of disulpharsenite of sodium gives, with neutral ferrous salts, a precipitate which is black-brown in the fresh state, and dissolves in an excess of the sodium-salt, forming a brownish-yellow solution. The precipitate, when dried, is converted into a greyish-brown mixture of ferric oxide and ferric sulpharsenite (K), and afterwards yields by distillation sulphurous acid and sulphide of arsenic, while sulphide of iron free from arsenic remains behind. (Berzelius.)

K. Ferric Sulpharsenite.—Ferric salts form with bibasic sulpharsenite of sodium—the liquid retaining a greenish colour—an olive-green precipitate, which dissolves in excess of the re-agent, forming a black solution. After drying, it fuses readily, and solidifies in the form of a yellowish translucent mass, which, as before fusion, yields a greenish-yellow powder. At a red heat, it leaves sulphide of iron free from arsenic. (Berzelius.)

L. Ferrous Sulpharseniate.—Dark brown precipitate, which soon turns black : it is produced on mixing a ferrous salt with the aqueous solution of either bibasic or terbasic sulpharseniate of sodium. It dissolves in excess of the sodium-compound, forming a black-brown solution. When dried in the air, it is resolved into a yellowish-brown mixture of hydrated ferric oxide and ferric sulpharseniate. (Berzelius.)

M. Ferric Sulpharseniate.—Both terbasic and bibasic sulpharseniate of sodium form dingy greenish-grey precipitates with ferric salts, the former more slowly than the latter, and an excess of either sodium-salt re-dissolves the precipitate, forming a black-brown solution. The precipitate, which does not decompose in drying, fuses very easily, and at a moderate heat gives off sulphur, and is converted into a compound containing tersulphide of arsenic, which is likewise easily fusible. (Berzelius.)

N. Proto-arsenide of Iron with Bisulphide of Iron.—*Arsenical Iron, Mispickel, Giftkies.* Crystalline system the right prismatic. Fig. 61 (primary form), 44, 54, and others. $u' : u=111° 18'$, $i : u=115° 32'$; i *above* : u *below*$=99° 36'$. Cleavage parallel to *a* and *p*. (Hauy.) Sp. gr. 6·13. Somewhat softer than felspar; gives a few sparks with steel, emitting an arsenical odour. Tin-white; powder blackish-grey. When heated in a flask, it first gives a red sublimate of sulphide of arsenic, then a black, and lastly a metallic-looking sublimate of arsenic, and leaves sulphide of

iron. Heated on charcoal before the blowpipe, it emits a strong arsenical fume, and fuses to a globule, which behaves like magnetic pyrites. (Berzelius.) Dissolves in strong nitric acid or aqua-regia, with separation of sulphur and arsenious acid.

161 parts (1 At.) of arsenical iron, placed in a crucible with a small quantity of borax, and heated in the blast-furnace, lose 72·45 pts.—viz. 1 At. sulphur and $\frac{3}{4}$ At. arsenic (16+56·25=72·25).—The residue, which is crystalline, brittle, strongly magnetic, and of a pale greyish-yellow colour, consists of FeS and Fe^4As. On boiling the mass with strong hydrochloric acid as long as sulphuretted hydrogen continues to go off, the Fe^4As remains behind in blackish-grey metallic scales (containing 59 p. c. iron and 41 arsenic). These grains, when boiled for a longer time, give up half their iron to the acid, with evolution of hydrogen gas, and the residue consists of Fe^2S (41·9 p. c. iron and 58·1 arsenic), on which the hydrochloric acid has no further effect. 4 At. arsenical iron contain 8Fe, 4As, 8S; $2AsS^3$ and 1As are evolved, and there remains 4FeS, together with Fe^4As. The mineral, when heated to whiteness in a charcoal crucible with six times its weight of lead, yields lead free from iron, but rendered somewhat brittle by the presence of arsenic and sulphur,—together with a dense, granular, yellowish-grey, strongly magnetic mass, which contains 67 p. c. iron, 25 arsenic, and 8 sulphur, and when boiled for some time with hydrochloric acid, leaves Fe^4As in the form of a black powder. (Berthier, *Ann. Chim. Phys.* 62, 113; also *J. pr. Chem.* 10, 13.)

Arsenical Iron.		At.			Chevreul. *Cryst.*	Stromeyer. *Cryst.* Freiberg.	Scheerer. Skutterud.	Wöhler.
Fe	2	54	33·54		34·94	36·04	26·62	30·91
Co							8·57	4·75
As	1	75	46·58		43·42	42·88	46·74	47·45
S	2	32	19·88		20·13	21·08	17·66	17·78
$FeAs, FeS^2$		161	100·00		98·49	100·00	99·59	100·89

Iron and Antimony.

A. Antimonide of Iron.—Regulus *Antimonii martialis.*—1. The two metals, when heated together, fuse into a mass with visible combustion. (Gehlen.)—2. When 177 pts. (1 At.) of grey sulphide of antimony are fused with more than 81 pts. (3 At.) of iron, antimonide of iron is obtained, besides sulphide of iron. Hard, brittle, slightly magnetic alloy, having a density below the mean given by calculation. The alloy of 1 pt. iron and 2 pts. antimony gives sparks when filed.

B. Ferrous Antimoniate.—Formed by double decomposition.—White powder, which becomes yellowish-grey by drying, and, at a red heat, gives off water and turns red. It is slightly soluble in water.—Similar characters are exhibited by the antimonite. (Berzelius.)

C. Ferric Antimoniate.—Light yellow. (Berzelius.)

D. Ferrous Sulphantimonite.—Protosulphide of iron may be fused in all proportions with tersulphide of antimony. (Berthier.)

The three following minerals are provisionally included under the *name Berthierite* or *Haidingerite;* if, however, satisfactory evidence of

a greenish yellow-brown precipitate is obtained, free from iron and consisting of a mixture of sulphur and pentasulphide of antimony, containing altogether 50 per cent. of sulphur; the filtrate contains a ferrous salt.

$$3NaS, SbS^5 + 3(Fe^2O^3, 3SO^3) = 3(NaO, SO^3) + 6(FeO, SO^3) + SbS^5 + 3S.$$

(Rammelsberg, *Pogg.* 52, 234.)

F. Antimonide of Iron and Potassium.—Formed by mixing 1 pt. of iron-turnings with 1½ pt. of pulverized antimony and 1 pt. of tartar, and exposing the mixture in a covered crucible to the heat of a powerful wind-furnace.—Brittle alloy, rich in potassium. (Serullas.)

Iron and Tellurium.

A. Telluride of Iron.—The compound obtained by reducing ferrous tellurite with hydrogen gas, dissolves in hydrochloric acid, with evolution of telluretted hydrogen. If the ferrous tellurite contains excess of acid, tellurium is immediately separated. (Berzelius.)

B. Ferrous Tellurite.—Formed by double decomposition. Yellowish-grey flakes. (Berzelius.)

C. Ferric Tellurite.—Fine yellow-coloured flakes. (Berzelius.)

D. Ferrous Tellurate. — White precipitate, which, on exposure to the air, soon turns greenish-grey, and afterwards rust-coloured. (Berzelius.)

E. Ferric Tellurate.—Pale yellow flakes, soluble in excess of the ferric salt. (Berzelius.)

F. Ferrous Sulphotellurite.—Black precipitate.

G. Ferric Sulphotellurite.—Dark brown flakes, which cake together into an easily fusible mass. This mass, when heated in a retort, gives off a large quantity of sulphur, and leaves a grey residue which exhibits the metallic lustre. (Berzelius.)

Iron and Bismuth.

A. Bismuthide of Iron.—Brittle alloy, which, even when it contains only a fourth part of iron, is attracted by the magnet (Henkel), and exhibits a decrease of density. (Gellert.)—Marx (*Schw.* 58, 471) did not succeed in forming an alloy of these two metals.

B. Bismuthide of Iron and Potassium.—Analogous to the antimonide.

Iron and Zinc.

A. Alloy of Iron and Zinc.—Combination takes place with difficulty.—When cuttings of zinc and iron are ignited together, part of the *zinc evaporates*, according to Gehlen, while the rest penetrates the iron

and makes it denser and very brittle.—2. Iron-filings ignited with zinc-oxide, but without charcoal and under a layer of pounded glass, take up a tolerably large quantity of zinc. (Hollunder.) — A vessel of either wrought or cast-iron in which zinc is continuously melted, becomes corroded by the formation of an alloy of zinc and iron. (Hollunder, *Schw.* 33, 41, and 166; Berthier, *Ann. Chim. Phys.* 44, 119; Elsner, *J. pr. Chem.* 12, 303.)—4. In the *zinking* of iron-plate by immersing it in melted zinc, with frequent addition of sal-ammoniac, an alloy of zinc and iron is deposited at the bottom of the fused zinc, in the form of a doughy mass, which is taken out from time to time. (Berthier, *Pogg.* 52, 340.)

The alloy α formed by (3) in cast-iron is whiter than zinc, and so much the more brittle and oxidable as it contains a larger quantity of iron. At a very high temperature, the whole of the zinc is evolved. (Hollunder.)—It consists of warty plates, easily detached from the sides of the vessel, having a crystalline, shining fracture, very hard and brittle, and less fusible than zinc; it gives off its zinc by distillation, and dissolves in nitric acid, only the graphite of the cast iron being left undissolved. (Berthier.)—It has a density of 6·7, a fine-grained fracture and tin-white colour. (Elsner.)—The alloy (4) has the outward appearance of zinc and is not magnetic, but harder and very crystalline. (Berthier.)—The alloy of zinc and iron formed in a wrought iron vessel in the process of zinking iron-plates (3,β) is so brittle, that it may be rubbed into crystalline grains with the fingers; it has the colour of zinc, and is very easily soluble in acetic acid even when cold. (Berthier.)

	Berthier. (3,a)		Elsner. (3,a)		Berthier. (4)		(3,β)
Zn	94·76	....	93·01	....	95·3	....	90·1
Fe	5·00	....	6·24	....	4·3	....	9·5
Graphite	0·24	....	0·75	Pb	0·4	....	0·4
				Cu	trace	....	
	100·00	....	100·00	....	100·0	....	100·0

B. Ferric Oxide with Zinc-oxide. — *Franklinite.* — (ZnO;FeO), (Mn^2O^3; Fe^2O^3).—Isomorphous with spinelle, &c. *Fig.* 2 and 4. Sp. gr. 5·09. Scratches apatite. Opaque, and of an iron-black colour; powder red-brown; magnetic, especially after ignition. Held between the platinum forceps in the outer blowpipe flame, it shines with a white light, attended with emission of sparks and the formation of minute blisters on the surface, which may be seen with a lens. On charcoal, by continued blowing, it is reduced to a black slag, with formation of a zinc-deposit. With carbonate of soda on platinum, it exhibits the re-action of manganese. Dissolves in borax, forming a red glass which turns brown on cooling. In microcosmic salt, it dissolves less readily and with strong intumescence, forming a yellowish-grey glass which easily assumes a milky appearance. Dissolves with difficulty in sulphuric or nitric acid; easily in hydrochloric acid, with copious evolution of chlorine. (Abich, *Pogg.* 23, 324.) The hydrochloric acid solution contains sesquioxide of iron with only a trace of protoxide. The evolution of chlorine is remarkable, and, as Kobell observes, is not consistent with the results of Abich's analysis; but the calculation given by Kobell (*Schw.* 64, 430) for removing this difficulty (see the following table) is unsatisfactory: for the 13·82 per cent. of sesquioxide of manganese therein assumed could only give up 1·382 p. c. oxygen; but the 18·37 p. c. of protoxide of iron likewise assumed requires 2·099 p. c. oxygen,—so that there is not even enough

oxygen to convert all the protoxide into sesquioxide, to say nothing of the quantity which would be required to liberate chlorine from the hydrochloric acid.—Might not another formula be assigned to Franklinite —perhaps $(ZnO; FeO), 2(Mn^2O^3; Fe^2O^3)$?

Franklinite.	Abich.	Berthier.	Kobell. *Calculation.*
ZnO	10·81	17	7·02
Mno			6·22
FeO	21·34		18·37
Fn^2O^3	18·17	16	13·82
Fe^2O^3	47·52	66	54·57
Al^2O^3	0·73		
SiO^3	0·40		
MgO.CdO	trace		
	98·97	99	100·00

C. Carbide of Iron and Zinc.—Formed by adding zinc to melted steel by small portions at a time, because larger quantities would produce explosion. The addition of $\frac{1}{50}$ part of zinc renders steel brittle. When the steel is forged, part of the zinc burns away. (Bréant.)

D. Sulphate of Ferrous Oxide and Zinc-oxide.—A mixture of ferrous sulphate and zinc-sulphate takes the crystalline shape of the former, if the quantity of that substance amounts to at least 15 per cent. of the whole; but if the quantity of ferrous sulphate be smaller, the mixed salt takes the form of zinc-sulphate.

E. Sulphate of Ferrous Oxide, Zinc-oxide, and Ammonia.—The mixed solution of ferroso-ammonic sulphate and zinco-ammonic sulphate yields pale green crystals which have the form of magnesio-ammonic sulphate, and assume a yellowish colour on exposure to the air. (Bette, *Ann. Pharm.* 14, 286.)

			Bette.
$2NH^3$	34·0	8·60	8·12
ZnO	40·2	10·17	9·10
FeO	35·0	8·86	10·35
$4SO^3$	160·0	40·49	40·03
14HO	126·0	31·88	32·40
	395·2	100·00	100·00

Iron and Tin.

A. Alloy of Iron and Tin.—When these two metals are heated to redness together, there is formed: *a.* An alloy of 22 pts. tin and 1 iron, somewhat harder than tin, and magnetic; and below it: *b.* A compound of 2 pts. iron and 1 pt. tin, which is white, very hard, slightly malleable, and difficult of fusion. (Bergman.)—*Tinned Iron-plate.*—In the daily distillation of the silvering of mirrors in a cast-iron retort for the purpose of regaining the mercury, an alloy of tin and iron is formed, amounting to between 1 and 2 per cent. of the tin obtained: when the tin is poured out of the retort, this alloy partly floats upon it in scales, and is partly deposited at the bottom in the form of a doughy mass. It may be freed from the pure tin which adheres to it, either by boiling with hydrochloric acid, which dissolves the latter, or by treating it with nitric acid, by which the free

tin is oxidized while the alloy is not attacked. When thus purified, it has the form of shining square needles, of specific gravity 8·733, brittle, and fusing at an incipient white heat. The powder of this compound, when thrown into the flame of a candle, burns with emission of sparks and a white smoke. It does not rust in the air, when moistened with water. It is not attacked by nitric acid at any temperature or any degree of concentration; it dissolves slowly in boiling hydrochloric acid; but rapidly and completely, and with violent action, in aqua-regia. (Lassaigne, *J. Chim. Méd.* 6, 609.)

					Lassaigne.
3Fe	81	....	57·86	....	57·9
Sn	59	....	42·14	....	42·1
Fe^3Sn	140	....	100·00	....	100·0

B. Carbide of Tin and Iron.—Tin impairs the quality of steel. (Faraday & Stodart.)

Iron and Lead.

Alloy.—The two metals unite with difficulty when fused together, forming two alloys, arranged one above the other, the lower containing but very little iron, and the upper but a very small quantity of lead. (Morveau.)—By reducing a slag containing lead and iron in a crucible lined with charcoal, Biewend (*J. pr. Chem.* 23, 252) obtained a well-fused alloy, which was hard, almost perfectly brittle, lustrous, and magnetic: it had a light steel-grey colour, a fine-grained laminar fracture, and contained 96·76 per cent. of iron and 3·24 of lead.

Other Compounds of Iron.

With Cobalt, Nickel, Copper, Mercury, Silver, Gold, Platinum, Palladium, Rhodium, and Osmium.

Chapter XXXIII.

COBALT.

G. Brandt, *Act. Upsal*, 1735, 33.
Tassaert, *Scher. J.* 3, 555, and 562.
Bucholz, *Scher. J.* 10, 10.
Thénard, *Scher. J.* 10, 422.
Proust, *Journ. Phys.* 63, 421; also *N. Gehl.* 3, 410.
Laugier, *Ann. Chim. Phys.* 9, 267; also *N. Tr.* 3, 2, 93.
Berzelius, *Pogg.* 1, 26, and 198; 7, 27, 146, 276, and 287.
Winkelblech, *Ann. Pharm.* 13, 148, and 253; also *J. pr. Chem.* 6, 62.

Synonymes. *Kobalt, Kobold, Cobaltum.*

History.—Many antique blue glass-fluxes (most of them are coloured with oxide of copper) contain oxide of cobalt. *Vid.* Fourier (*Ann. Chim. Phys.* 79, 378). Cobalt is likewise found in the colours of the ancient Greeks. (Landerer, *Repert.* 73, 380.) From the sixteenth century, ores of cobalt have been used for the preparation of smalt. Brandt, in 1733, first extracted the metal from its ores, though in an impure state.

Sources.—Cobalt is not very abundant; it occurs in meteoric-iron; as sulphate of the protoxide; as arseniate of the protoxide (*Cobalt-bloom*); as a compound of peroxide of manganese with protoxide of cobalt (*Black Earthy Cobalt*); as arsenide of cobalt (*Tin-white cobalt* or *Smaltine*); as sulpharsenide of cobalt (*Cobalt-glance*). Moreover, it occurs in very small quantities in other minerals, *e. g.* in Selenide of Lead, in Cerite (Berzelius, *Jahresber.* 15, 214), and in Flemish coal. (Kuhlmann, *Ann. Pharm.* 38, 45.)

Preparation.—Principally from Tin-white cobalt and Cobalt-glance, and the impure arseniate obtained by roasting these ores. The roasted product generally also contains bismuth, tin, copper, manganese, nickel, and iron in the state of oxides; when prepared on the large scale, it is mixed with twice its weight of quartz-sand, and put into casks, and in that state is sent into the market under the name of *Zaffra*, *Zaffer*, or *Safflor*. The Cobalt-glance and Tin-white cobalt are usually dissolved in nitric acid, or in dilute sulphuric or hydrochloric acid to which a little nitric acid has been added; the thoroughly roasted ore (which, however, is more difficult to dissolve than before roasting) and Earthy cobalt do not require the addition of nitric acid.

1. The roasted cobalt-ore is dissolved in nitric acid; the filtered solution evaporated nearly to dryness, whereupon a large quantity of arsenious acid separates out; the liquid largely diluted, separated from the arsenious acid, and treated with sulphuretted hydrogen as long as

the sulphides of arsenic, copper, and bismuth (together with tin) continue to be precipitated. The solution is then filtered, and heated till the excess of sulphuretted hydrogen is expelled and the protoxide of iron converted into sesquioxide; and carbonate of soda is added in excess, while the liquid is hot, to precipitate the nickel and cobalt in the form of carbonates, and the iron in the form of sesquioxide. The precipitate is then well washed and digested with excess of aqueous oxalic acid; the soluble ferric oxalate separated by filtration from the oxalates of nickel and cobalt, which are insoluble even in excess of oxalic acid, and the latter salts triturated with dilute ammonia (it should be strong ammonia according to Stromeyer) and dissolved in excess of the ammonia, by agitation and gentle heating in a close vessel. The filtered solution, after exposure to the air for several days, deposits the oxide of nickel in combination with oxalic acid and a small quantity of ammonia, while pure oxalate of cobalt remains in solution. (The oxalate of nickel separated as above may be freed from the small quantity of cobalt-salt which falls down with it, by washing with water, re-dissolving in ammonia, exposing the liquid to the air, and separating the solution which contains the cobalt from the nickel-precipitate, the purity of which increases at each repetition of the process.) The residue obtained by evaporating the ammoniacal solution of the oxalate, yields sesquioxide of cobalt when ignited in the air, and metallic cobalt if ignited out of contact of air. (Laugier.) The liquid, after precipitation by sulphuretted hydrogen, may also, after sufficient boiling, be diluted with a large quantity of water and gradually mixed with carbonate of soda (Stromeyer's process), stirring all the while, till the precipitate is no longer red-brown, but permanently red*; if the proportion be rightly adjusted, the whole of the ferric oxide is precipitated, and the protoxides of nickel and cobalt remain in the solution, from which they may be precipitated by boiling with excess of carbonate of soda, and treated with oxalic acid, according to Laugier's method.

2. Unroasted cobalt-ore is dissolved in nitric acid; the solution evaporated to dryness; the residue dissolved in water; carbonate of soda added with constant agitation to the diluted filtrate, till the cobalt begins to fall down together with the other metals (this will be indicated by the red colour of the precipitate); the liquid filtered from the arseniate of ferric oxide; and a hot saturated solution of acid oxalate of potash added to it. The whole of the cobalt is thereby precipitated in a few hours, in the form of oxalate, while all the iron and arsenic, and the greater part of the nickel, remain in solution. Should the precipitate likewise contain arseniate of cobalt-oxide, the latter may be removed by dilute nitric acid, in which the acid oxalate is not soluble. The oxalate may be freed from nickel by Laugier's process (1); since, however, the quantity of nickel is but small, it may likewise be extracted by digesting the precipitate in a small quantity of hot aqueous ammonia which dissolves the nickel-oxalate in preference to the cobalt-oxalate, and forms a blue solution. (Quesneville, *J. Pharm.* 15, 291, and 441.) The filtrate, after being mixed with the acid oxalate of potash, should be boiled in order that the cobalt-

¶ * A modification of this method, which consists in mixing the cobalt solution with gelatinous hydrate of cobalt oxide, or partially precipitating it with carbonate of potash or soda, and then boiling for some time—whereby the iron is completely precipitated, and the cobalt takes its place in the solution—is recommended by Louyet (*Instit.* 1849, 206).—The same method has long been used for the separation of manganese from iron.

oxalate may settle down more quickly; the precipitate is contaminated with a small quantity of cupric oxalate, which, after ignition and solution in hydrochloric acid, may be removed by sulphuretted hydrogen. (Hess, *Pogg.* 26, 542.)

3. The nitric acid solution of the roasted ore, after being filtered and diluted with a proper quantity of water, is saturated with hydrosulphuric acid—filtered again—boiled—precipitated by carbonate of potash—filtered from sesquioxide of iron, and diluted with water; a small quantity of sal-ammoniac is now added, then potash, and the liquid is boiled till a filtered sample no longer gives a precipitate with potash. The red cobalt-solution is then filtered off, and yields sesquioxide of cobalt on evaporation. (Wittstein, *Repert.* 57, 226.)

4. To avoid the tedious passing of sulphuretted hydrogen through the liquid, the arsenic acid may be precipitated by first mixing the dilute solution with a ferric salt, and then adding carbonate of potash in small successive portions and with constant agitation, as long as the precipitate continues to exhibit a white or brownish colour (arseniate of ferric oxide); till, in short, a filtered sample of the liquid gives a reddish precipitate with a small quantity of carbonate of potash. If the quantity of ferric oxide be sufficient, and the proportion of carbonate of potash rightly adjusted, the whole of the arsenic acid and ferric oxide may be precipitated. If the copper and bismuth be then removed by sulphuretted hydrogen, it only remains to separate the nickel from the cobalt. (Berthier.)

5. Finely pounded cobalt-ore is carefully roasted, and 1 pt. of it added in successive small portions to 3 pts. of bisulphate of potash heated to the melting point in an earthen or cast-iron crucible. The mass, which is thereby rendered pasty, is then more strongly heated till it fuses quietly and no longer gives off fumes of sulphuric acid, as it is necessary to drive away the excess of that acid. The mass, while yet liquid, is then taken out of the crucible with an iron spoon—broken to pieces after cooling—dissolved in boiling water, and filtered from the arseniates of ferric oxide and cobalt-oxide, which are not soluble in a neutral liquid. Sulphuretted hydrogen is then passed through the filtrate to throw down any antimony, bismuth, or copper that may be present—the liquid again filtered, and pure carbonate of cobalt-oxide precipitated by carbonate of potash. To prevent the formation of arseniate of cobalt-oxide, the roasted cobalt-ore, before fusion with sulphate of potash, may be mixed with a small quantity of green vitriol, so that the arsenic acid may combine with the oxide of iron contained in that salt in preference to the oxide of cobalt. No nickel is taken up by the liquid, because the nickel-sulphate is decomposed at a red heat [not so, however, the sulphate of nickel-oxide and potash, unless the heat applied is very strong]. The solution retains but a trace of iron at the utmost. (Liebig, *Pogg.* 18, 164.)

6. One part of pulverized Tin-white cobalt or Cobalt-glance is fused in a covered earthen crucible with 3 pts. of carbonate of potash and 3 pts. of sulphur, at so gentle a heat that the sulphide of cobalt does not fuse, but remains in the form of a crystalline powder (if it fuses it becomes more difficult to wash). It is then freed from sulpharseniate of potassium by repeated exhaustion with water and decantation; again treated with carbonate of potash and sulphur, and then with water to remove the rest of the arsenic; afterwards dissolved in nitric acid or in *dilute sulphuric* acid mixed with nitric; and the solution precipitated

with carbonate of soda. (Wöhler, *Pogg.* 6, 227.) According to Hermbstadt (*Schw.* 31, 105), the greater part of the arsenic may likewise be removed by deflagrating the cobalt-glance with 3 pts. of nitre, and exhausting the fused mass with hot water. The remainder is then to be dissolved in hot nitric acid, whereupon, a small quantity of ferric oxide remains undissolved—the copper precipitated by iron—the liquid supersaturated with carbonate of ammonia—filtered from the iron precipitate—concentrated by evaporation, during which process a considerable quantity of iron is precipitated—then again filtered, and evaporated to perfect dryness, and the residue ignited.

7. To obtain cobalt from the black earthy cobalt-ore, the mineral is dissolved in hydrochloric acid; the arsenic, antimony, lead, and copper precipitated by sulphuretted hydrogen; the filtrate boiled with nitric acid to promote the further oxidation of the iron; the iron precipitated by boiling with acetate of soda; and the cobalt separated from the filtrate by sulphuretted hydrogen, which leaves the acetate of manganous oxide undecomposed. The precipitate is perfectly free from nickel, but contains a trace of zinc. The liquid, freed from arsenic and copper by sulphuretted hydrogen, may likewise be precipitated by sulphide of potassium or sulphide of barium, and the washed precipitate treated with cold, dilute hydrochloric acid, which dissolves the sulphides of manganese, zinc, and iron, and leaves all the sulphide of cobalt undissolved. (Wackenroder, *N. Br. Arch.* 16, 133.)

Special modes of separation from particular metals:

a. From Nickel.—1. By oxalic acid and ammonia according to Laugier's method 1. (p. 317.)—2. The solution of the two oxides in excess of acid is supersaturated with ammonia, diluted with a large quantity of water, and mixed with caustic potash, which precipitates the oxide of nickel; on evaporating the filtrate, the cobalt separates in the form of sesquioxide. (Phillips.)—If the water has not been sufficiently freed from air by boiling, or if the liquid, after the addition of potash, is not kept in a closed vessel, sesquioxide of cobalt is precipitated together with the oxide of nickel. (Berzelius.)—3. The nitric or hydrochloric acid solution of the two oxides is mixed with a quantity of metaphosphoric acid sufficient to saturate them, and ammonia added till the precipitate at first produced is re-dissolved, after which the mixture is exposed to the air for a considerable time. (Persoz, *Ann. Chim. Phys.* 56, 333; also *Pogg.* 33, 346.)—4. Since cyanide of nickel and potassium is decomposed by acids, and cyanide of cobalt and potassium is not, the separation may be effected by adding cyanide of potassium to the acidulated solution of the two metals, till the precipitate re-dissolves, heating gently to induce the formation of sesquicyanide of cobalt and potassium, mixing the liquid, after cooling, with dilute sulphuric acid, and filtering. The filtrate contains pure cobalt in the form of cyanide of cobalt and potassium: it is mixed with nitre, evaporated and ignited, and the residue exhausted with water, which leaves the cobalt in the form of sesquioxide. The precipitate on the filter consists of sesquicyanide of cobalt and nickel; it may be decomposed by caustic potash or carbonate of potash into soluble cyanide of cobalt and potassium, and insoluble hydrate or carbonate of nickel-oxide. (Liebig, *Ann. Pharm.* 41, 291.)—5. The oxides of the two metals are made to combine with sulphuric acid and potash, and the solution left to crystallize, whereupon the less soluble sulphate of nickel-oxide and potash separates out first, and the sulphate of cobalt-oxide and potash

remains in solution. (Proust.) Repeated crystallization is, however, often necessary to separate the whole of the nickel-salt from the cobalt-salt (the purification is complete when the mother liquid of the nickel-salt exhibits a pure green colour), and to free the whole of the cobalt solution from admixture of nickel-salt.

¶. Liebig's mode of separation by cyanide of potassium and hydrochloric or sulphuric acid has since been found, both by himself and others, not to give perfectly satisfactory results. Thus, T. H. Henry (*Chem. Gaz.* 1847, 170) finds that a solution of cyanide of cobalt and potassium boiled for some time with hydrochloric acid, or evaporated nearly to dryness with sulphuric acid, gives off hydrocyanic acid, and is decomposed in such a manner, that alkalis afterwards produce in it a precipitate of sesquioxide of cobalt: hence the nickel-salt obtained by method (4) always contains cobalt. The following method, likewise devised by Liebig, is free from this objection, and gives perfectly satisfactory results. —6. The oxides of the two metals are treated with hydrocyanic acid, then with potash, and the liquid warmed till the whole is dissolved; (pure cyanide of potassium free from cyanate of potash may likewise be used). The reddish-yellow solution is heated to the boiling point to expel the free hydrocyanic acid, whereupon the protocyanide of cobalt and potassium ($CoCy,KCy$) is converted into the corresponding sesqui-compound ($Co^2Cy^6,3K$), and the nickel remains in the solution in the form of cyanide of nickel and potassium. Pure protoxide of mercury, reduced to a very fine powder by levigation, is then added to the solution while yet warm, whereby the whole of the nickel is precipitated, partly as oxide, partly as cyanide, the mercury taking its place in the solution. If the liquid was neutral before the addition of the mercuric oxide, it becomes alkaline when boiled with that substance. The precipitate contains the whole of the nickel with excess of mercuric oxide: after washing and ignition, it yields pure oxide of nickel free from cobalt. The filtered liquid contains all the cobalt in the form of sesquicyanide of cobalt and potassium. It is supersaturated with acetic acid, and precipitated at a boiling heat with blue vitriol, and the precipitate, which consists of cyanide of cobalt and copper ($Co^2Cy^6,3Cu,7HO$), kept at that temperature in the liquid, till it has lost its glutinous character. It is then washed, dried, and ignited; dissolved in hydrochloric acid, to which a small quantity of nitric acid is added; the copper precipitated by sulphuretted hydrogen; and the liquid—after boiling for a minute to expel the sulphuretted hydrogen—mixed with boiling caustic potash to precipitate the cobalt. The precipitate, well washed to free it from potash, and afterwards dried and ignited, yields pure sesquioxide of cobalt.* (Liebig, *Ann. Pharm.* 65, 244; L. and K. *Jahresber.* I., 971.)

7. A solution of protochloride of cobalt mixed with free hydrochloric acid, is completely converted into sesquichloride by the action of chlorine gas, whereas the chloride of nickel remains unaltered when treated with that agent. The solution of the mixed chlorides containing a considerable quantity of free hydrochloric acid is largely diluted with water, and

* In applying this method to quantitative analysis, the cobalt may either be determined directly by separating the oxide in the manner just described, and then reducing it by hydrogen;—or the precipitate of cyanide of cobalt and copper may be digested in caustic potash, which will dissolve the cobalt, and leave the copper in the form of cupric oxide, and from the quantity of the latter, that of the cobalt may be calculated. A still greater simplification may be made by weighing the mixed oxides (or the mixed metals *reduced by hydrogen*) before applying the process of separation, and then merely determining the quantity of the nickel.

chlorine gas passed through it, till the liquid is completely saturated and the upper part of the vessel filled with the gas. Carbonate of baryta is then added in excess; the whole left to stand in the cold for 12 or 18 hours and frequently agitated; and the precipitated sesquioxide of cobalt, together with the excess of carbonate of baryta, collected on a filter. The precipitate, after washing with cold water, is dissolved in hot hydrochloric acid; the baryta removed by sulphuric acid; and the cobalt precipitated, in the form of protoxide, by caustic potash. The liquid filtered from the sesquioxide of cobalt and carbonate of baryta contains nothing but baryta and nickel; the baryta may be precipitated by sulphuric acid, and then the nickel by caustic potash. (H. Rose, *Pogg.* 71, 545; *Ann. Pharm.* 64, 411.) ¶

b. From Manganese.—1. The acid solution supersaturated with ammonia, deposits the greater part, but not the whole, of the manganese, in the form of black oxide.—2. The protoxides of the two metals are precipitated by boiling with carbonate of soda, the precipitate washed, and then heated with solution of potash and hydrocyanic acid. Part of the manganese remains undissolved: the solution contains cobalt in the form of cyanide of cobalt and potassium, together with cyanide of manganese and potassium. The latter is decomposed, with separation of manganic oxide, by repeatedly evaporating the solution to dryness and re-dissolving in water; the former remains unaltered, and may be removed by filtration. (Gmelin.)—The solution of the mixed oxides is treated as in the fourth method (Liebig's) of separating cobalt from nickel; on supersaturating with cyanide of potassium, the greater part of the manganese remains undissolved in the form of cyanide; the filtrate is decomposed, as already described, by dilute sulphuric acid. (Liebig.)—4. The acid solution of the two metals is mixed with a quantity of acetate of soda sufficient to convert the whole of the cobalt and manganese into acetates; the cobalt precipitated by sulphuretted hydrogen; and the sulphide of cobalt washed with sulphuretted hydrogen water to prevent the cobalt from oxidizing and re-dissolving. The whole of the manganese remains in solution; if, however, the acetic acid is in very great excess, the filtrate may still contain a small quantity of cobalt; if so, the excess of acid must be expelled by evaporation, and the remainder of the cobalt precipitated by again treating the liquid with sulphuretted hydrogen.—Or the solution of the two metals, not containing too great an excess of acid, may be precipitated by sulphide of ammonium, and acetic acid (or hydrochloric: *H. Rose*) added in excess; the sulphide of manganese will then dissolve, and, after a few minutes, the sulphide of cobalt may be thrown on a filter. Should the filtrate yield with sulphide of ammonium a black instead of a flesh-coloured precipitate, the process of separation must be repeated. (Wackenroder, *N. Br. Arch.* 16, 130.) — ¶ 5. The oxides of the two metals are precipitated from the mixed solution by caustic potash, then washed and dried, and afterwards heated to low redness in a tube through which a stream of sulphuretted hydrogen is passed, the flow of gas being continued till the tube is cold. The oxides are thereby converted into sulphides, which are then digested for some hours in cold water acidulated with hydrochloric acid; the manganese dissolves and the sulphide of cobalt is left behind. The same method may be applied to separate nickel from manganese. (Ebelmen, *N. Ann. Chim. Phys.* 25, 92.) ¶

The reduction of the protoxide or sesquioxide is effected: 1. In a crucible lined with charcoal—more easily indeed than that of the refrac-

tory, brittle metals, or of iron (the oxide should be covered with a glass-flux,—consisting of alumina and lime: Berthier, *Ann. Chim. Phys.* 25, 68.) —2. According to Clarke, in the flame of his oxy-hydrogen blowpipe.—3. By passing hydrogen gas over the oxide at a red heat.—4. By heating the oxalate to whiteness in a crucible, under a covering of glass, not containing any heavy metal. (Berzelius.)—By heating the oxalate of cobalt-oxide and ammonia in a closed crucible in a flame urged by the bellows. (Brunner, *Kastn. Arch.* 14, 176.)

Properties. Specific gravity 7·7 (Bergman), 8·5131 (Berzelius), 8·485 (Brunner), 8·5385 (Tassaert and Hauy), 8·7 (Lampadius).—¶ Rammelsberg, in five experiments with cobalt reduced by hydrogen, found the specific gravity to vary from 8·132 to 9·495; mean 8·957. ¶ —Tolerably hard; the metal obtained by (2) is somewhat malleable (Clarke); as malleable as cast-iron, and has a fibrous fracture (Berthier); may be flattened to a certain extent under the hammer, then flies to pieces and exhibits a granular fracture (Brunner). When it contains charcoal, arsenic, manganese, &c., it is brittle, and has either a fine-grained, or a somewhat laminar texture. Reddish grey, with faint metallic lustre.—When obtained by (3) it forms a grey powder.—Fuses more easily than iron, less easily than gold.—It is magnetic. According to Wollaston (*Schw.* 42, 237), the magnetism of cobalt is to that of iron as 5 or 6 to 8 or 9; according to Lampadius (*Schw.* 10, 174), that of cobalt not perfectly pure is to that of iron as 25:55. According to Faraday (*Pogg.* 47, 219), pure cobalt is not at all magnetic, not even at a degree of cold about as low as—80°.C.

Compounds of Cobalt.

Cobalt and Oxygen.

A. Cobalt-oxide or Cobaltous Oxide. CoO.

Protoxide of Cobalt, Kobaltoxydul; formerly *Kobaltoxyd.—Formation.* —1. Cobalt in the coherent state does not oxidize in the air at ordinary temperatures; at a red heat, it is slowly converted into protoxide and afterwards into cobaltoso-cobaltic oxide; when intensely heated, it burns with a red light. According to Magnus and W. Henry, cobalt reduced at a gentle heat by (3) burns in the air at ordinary temperatures; and, according to Hess, that which has been reduced at a red heat gradually absorbs oxygen from the air. The product of these combustions is sometimes the protoxide, sometimes the sesquioxide of cobalt.—2. Red-hot cobalt decomposes vapour of water, hydrogen gas being evolved and protoxide of cobalt formed. (Despretz; Regnault, *Ann. Chim. Phys.* 62, 351.) Cobalt decomposes water when mixed with hydrochloric or sulphuric acid; it decomposes oil of vitriol with evolution of sulphurous acid gas, and easily decomposes nitric acid with evolution of nitrous gas. In all these reactions, the product is protoxide of cobalt united with the acid.

Preparation.—1. By igniting the pulverulent metal obtained by (3) in an open platinum crucible. (Winkelblech.)—2. By passing hydrogen gas over the hydrated oxide heated to a temperature not exceeding 350°. *The hydrate* may be heated in a glass globe placed in the mercury-bath;

at a higher temperature, reduction would take place. (Winkelblech.)—3. By gently heating the hydrate or carbonate out of contact of air: *e. g.* in a tube completely filled with it and drawn out to a point. (Winkelblech.)—The oxide must be preserved in a sealed tube, as it gradually turns brown when exposed to the air. (Winkelblech.)

When half a gramme of sesquioxide of cobalt, and 2 or 3 grammes of hydrate of potash, are placed together in a silver crucible and heated for some minutes to commencing redness, and the mass, after cooling, digested in water, the protoxide remains in the form of square tables. (Becquerel, *Ann. Chim. Phys.* 51, 105.)—It generally takes the form of a light greenish-grey (Proust), or olive-green (Winkelblech), non-magnetic powder.

	Calculation, according to Rothoff.			Berthier.	Proust.
CO	29·5	78·67		78·75	84
O	8·0	21·33		21·25	16
CoO	37·5	100·00		100·00	100

Decompositions.—Reduced to the metallic state at high temperatures by hydrogen, charcoal, carbonic oxide, potassium, and sodium. At the temperature at which cobalt-oxide is reduced by hydrogen, the metallic cobalt likewise decomposes the excess of aqueous vapour. (Despretz.) A mixture of carbonic oxide and carbonic acid gases in equal volumes, likewise reduces cobalt completely from the protoxide, and has therefore no action on metallic cobalt. (Laurent.)—Heated with carbonate of soda on charcoal in the inner blowpipe-flame, protoxide of cobalt is easily reduced to the metallic state, and, on washing away the soda and charcoal, the reduced metal is left in the form of a grey magnetic powder. (Berzelius.)—Protoxide of cobalt, heated with sulphur, is converted into sulphide of cobalt and sulphurous acid; heated with sulphuretted hydrogen, it yields water and sulphide of cobalt.

Combinations. — *a.* With Water. — HYDRATED COBALT-OXIDE or COBALT-HYDRATE.—Formed by decomposing a cobalt-salt with strong caustic potash, out of contact of air. The blue colour of the precipitate changes first to violet, and then to rose-colour, the change being greatly accelerated by boiling. (Proust.)—On throwing a crystal of cobalt-sulphate or nitrate into a bottle filled with caustic potash, and then closing the bottle, a blue precipitate is formed, which soon turns violet, and afterwards rose-red. If the cobalt-solution be dropped into the boiling potash-ley, the change of colour is almost too rapid to be traced. On boiling the hydrated carbonate with potash-ley, the protoxide is first produced in the form of a bulky, blue mass, which afterwards assumes a violet colour, and is ultimately converted into the rose-coloured hydrate. (Proust.) The potash-ley and the cobalt-solution should both be freed from air by boiling before they are mixed. (Winkelblech.) According to Winkelblech, the precipitate may be washed and dried in the air without change of colour, excepting that a brown tinge comes over it during drying; according to Proust, however, it becomes brownish if exposed to the air in the moist state, and is finally converted into the brown hydrated sesquioxide.

Rose-coloured powder (Winkelblech); brownish rose-coloured (Proust).—Gives off its water when heated above 100°.

					Winkelblech.				Proust.		
CoO	37·5	....	80·64	....	80·15	to	80·69	....	80	to	79
HO	9·0	....	19·36	....	19·53	,,	19·13	....	20	,,	21
CoO,HO	46·5	....	100·00	....	99·65	,,	99·82	....	100	,,	100

b. With Acids, forming the SALTS OF COBALT-OXIDE OR COBALT-SALTS*.—These salts are obtained by dissolving the metal in the stronger acids; by treating the protoxide or carbonate with acids; by double decomposition, &c. The hydrated oxide and carbonate likewise dissolve in sulphate, hydrochlorate, nitrate, and succinate of ammonia (Brett, Wittstein) with evolution of ammonia on boiling. (Demarçay.) The insoluble cobalt-salts are peach-blossom coloured or violet; the soluble salts, carmine-coloured. Those which contain a volatile acid part with it when ignited; the sulphate, however, is but partially decomposed. With carbonate of soda, borax, and microcosmic salt before the blowpipe, cobalt-salts exhibit the same phenomena as the oxide itself. Zinc and cadmium are the only metals which precipitate cobalt from its solutions in the metallic state.—These metals do not precipitate cobalt completely from its solution in hydrochloric acid, even when the action is continued for a long time; and on the nitric acid solution they exert no action whatever. (N. Fischer, *Pogg.* 9, 266.)

Sulphuretted hydrogen forms no precipitate in solutions of cobalt-oxide in the stronger acids, if these acids are but the least degree in excess; but if the stronger acids are completely saturated, the greater part of the cobalt is precipitated in the form of black hydrated sulphide; from a solution in the weaker acids, such as acetic acid, sulphuretted hydrogen throws down the whole or the greater part of the cobalt.—When sulphate, hydrochlorate, or nitrate of cobalt-oxide, is converted into acetate by the addition of acetate of soda, the cobalt is completely precipitated by sulphuretted hydrogen, excepting that when the excess of acetic acid becomes very large, a small portion of cobalt remains in solution: this, however, may be completely precipitated by sulphuretted hydrogen after the excess of acid has been driven off by boiling. Sulphide of cobalt, when once precipitated, is but sparingly redissolved by sulphuric, hydrochloric, or nitric acid,—still less by strong acetic acid added in excess: hence, a very small quantity of an alkaline hydrosulphate added to a very acid cobalt-solution produces a permanent precipitate. (Wackenroder, *N. Br. Arch.* 16, 129.)—Alkaline hydrosulphates completely precipitate all cobalt-salts, yielding the same brown-black, hydrated sulphide of cobalt, and dissolve but very little of it when added in excess. The precipitate is likewise insoluble in caustic alkalis. The brown-colouring is apparent, even in a solution diluted to 200,000 parts. (Pfaff.)—Hydrated sulphide of manganese likewise throws down hydrated sulphide of cobalt from solutions of cobalt-salts. (Anthon.)

Ammonia added in excess to a cobalt-salt, containing either a salt of ammonia or a large quantity of free acid, by which the first portions of ammonia are converted into an ammoniacal salt, yields a clear red mixture, which, on exposure to the air, turns brown from above downwards, and generally deposits brown, hydrated sesquioxide of cobalt.—If the cobalt-solution contains neither ammoniacal salt nor free acid, part

* As the salts of Cobaltic oxide (Co^2O^3) are not of much importance, and the termination *ous* rather implies inferiority in point of stability, I have thought it better to designate the salts of the protoxide by the simpler term, *Cobalt-salts*, rather than by *that of Cobaltous* salts, excepting in the few cases in which they are mentioned in the *same sentence* with the salts of the sesquioxide. [W.]

of the oxide is immediately precipitated (as basic salt) in blue flakes, which remain blue for some time if kept from the air, and afterwards change into the red hydrate, in a few hours at ordinary temperatures, but more quickly if the mixture be boiled; if, on the contrary, the air has access to them, they quickly turn green, and then either assume a brown colour, or dissolve and form a brown solution.—If the cobalt-solution be completely freed from air by boiling, and the air be perfectly excluded after the ammonia has been added, the blue precipitate, which is a basic salt, is converted, very slowly in the cold, but more quickly when heated, into the red hydrate; but on the slightest access of air, it assumes a green colour. (Winkelblech.) For further details vid. *Cobalto-nitrate of Ammonia* (p. 342).

Caustic potash added to cobalt-salts, out of contact of air, throws down blue flakes, consisting, according to Proust, of finely-divided cobalt-oxide, or, according to Winkelblech, of a basic salt; they are converted, slowly at ordinary temperatures, but quickly when heated, into the rose-coloured hydrate, which is also immediately formed if the liquids are mixed hot. It is advisable, before mixing the liquids, to expel the air from both of them by boiling, so as to obtain, first a pure blue, and afterwards a pure rose-coloured precipitate. (Winkelblech.) If the air has access to the liquid, the blue flakes change colour—in consequence of the formation of the hydrated oxide or of a basic salt—becoming, first olive-green, and afterwards partially of a dirty violet colour. In an aqueous solution of protochloride of cobalt mixed with a large quantity of sal-ammoniac, potash produces no precipitate if the air has been completely driven off by boiling; in the contrary case, a slight brown precipitate is formed. If the quantity of sal-ammoniac be smaller, potash produces a blue precipitate, and the liquid assumes a brown tint if any sal-ammoniac remains undecomposed, or a rose colour if the sal-ammoniac has been decomposed by considerable quantities of potash. (Winkelblech.)

Carbonate of ammonia, potash, or soda, produces in cobalt-salts a pale, peach-blossom-coloured precipitate of carbonate of cobalt-oxide; this precipitate is easily soluble in excess of carbonate of ammonia, yielding a solution of the same colour; it is also soluble, though very sparingly, in a large excess of strong carbonate of potash or soda. The precipitate turns blue when boiled with the carbonate of potash or soda; it does not disappear on passing chlorine gas through the liquid, but is converted into black, hydrated sesquioxide of cobalt. According to Fuchs (*Schw.* 62, 181) and Winkelblech, cobalt-salts are not precipitated by heating with carbonate of lime or boiling with carbonate of strontia. According to Demarçay (*Ann. Pharm.* 11, 240), the carbonates of baryta, strontia, lime, and magnesia, though they do not precipitate cobalt-salts in the cold, nevertheless decompose them completely at temperatures above 75°; the precipitation of cobalt-salts by carbonate of magnesia, and more quickly by pure magnesia, has likewise been observed by Döbereiner. (*Schw.* 63, 432.)—Phosphate of soda yields a blue precipitate of phosphate of cobalt-oxide.—Sulphite of potash (but not sulphite of ammonia) boiled with a cobalt-solution, throws down part of the oxide in the form of basic sulphite. (Berthier.)—Solution of silica gives a blue precipitate with cobalt-salts, and colours them blue, even when so far diluted that potash has no effect on them. (Fuchs.)—The hydrated protoxides of tin and lead, and protoxide of mercury, completely precipitate protochloride of cobalt at a boiling heat. (Demarçay.)

Oxalic acid produces turbidity in cobalt-solutions after a while, and

gradually throws down nearly all the cobalt in the form of pale rose-coloured oxalate: the same precipitate is produced by alkaline oxalates (even in solution 1000 times diluted: Pfaff). Ferrocyanide of potassium produces a green, and ferricyanide of potassium, a thick brown-red precipitate insoluble in hydrochloric acid. Tincture of galls produces a light red-brown precipitate in the solution of the acetate, but not in the solutions of cobalt in the stronger acids, except on the addition of acetate of potash.

c. With Alkalis.

d. With some of the Earths and Heavy Metallic Oxides.

B. Cobaltoso-cobaltic Oxide.

a. $Co^5O^9 = 6CoO, Co^2O^3$.—The *Hydrate.*—Formed by precipitating neutral nitrate of cobalt-oxide with ammonia—exposing the liquid to the air till the blue precipitate turns green—then diffusing the precipitate in water, and exposing it to the air for a month, till it turns quite yellow. The yellow hydrate thus formed still contains a trace of nitric acid, which cannot be removed even by long contact with water.

b. $Co^6O^7 = 4CoO, Co^2O^3$.—Formed by keeping the hydrated protoxide at a red heat in the air for a considerable time—or by first reducing it to the metallic state by heating it very gently in a tube through which hydrogen gas is passed, and then burning it again by passing air through the tube.—Soft, velvet-black powder. (Winkelblech.)

			Winkelblech (*mean*).
6Co	177	75·96	75·82
7O	56	24·04	24·06
Co^6O^7	233	100·00	99·88

¶ According to Rammelsberg (*Pogg.* 78, 93) the oxide formed by igniting the hydrate, carbonate, or oxalate of the protoxide at a moderate red heat is not Co^6O^7 but Co^3O^4. The residue afforded by the hydrate contained 74·28 p. c. of cobalt; that of the carbonate, from 72·69 to 74·44; that of the oxalates from 73·62 to 74·33 p. c. The formula Co^3O^4 requires 73·46 per cent. At a higher temperature, Co^6O^7 is formed ¶.

c. $Co^3O^4 = CoO, Co^2O^3$.—Formed when the nitrate or oxalate of the protoxide is ignited in the air either gently or strongly, or when the hydrated sesquioxide is gently ignited (Hess); when the sesquioxide is heated to low redness; and when the hydrated sesquioxide is heated not quite to redness. (Winkelblech.)—Resembles the preceding compound. Forms a peculiar salt with oxalic acid. (Winkelblech.)

			Hess.	Winkelblech (*mean*).
3Co	88·5	73·44	73·57	72·20
4O	32·0	26·56	26·43	26·41
Co^3O^4	120·5	100·00	100·00	98·61

C. Cobaltic Oxide. Co^2O^3.

Sesquioxide of Cobalt, Kobaltoxyd: formerly Peroxide of Cobalt, Kobalt-hyperoxyd.—1. Formed by gently igniting the nitrate of the protoxide. (Proust.)—When this salt is fused, blackish-grey metallic-looking particles separate from it, till the whole is converted into a steel-grey mass. To expel the remainder of the nitric acid from this substance, it is finely pounded and gently heated in a porcelain crucible as long as

red vapours continue to go off. It is difficult to drive off the whole of the nitric acid; for it is very forcibly retained, and at a very high temperature, the sesquioxide is converted into Co^3O^4. (Winkelblech.)—2. By decomposing chloride of cobalt in the dry way with carbonate of soda, and washing the residue with water. (Hess, *Pogg.* 26, 542.)—According to earlier statements, the sesquioxide is produced when the metal or its protoxide is gently ignited in the air; according to Proust, the carbonate heated in a covered crucible takes fire immediately on opening the crucible; but according to Hess and Winkelblech, the product in these cases is only Co^3O^4.

Brownish-black. As obtained by (2), it forms a brown powder which acquires a waxy lustre by friction with a hard body. (Hess.)—At a low red heat, it gives off oxygen and is converted into Co^3O^4. (Hess, Winkelblech.) According to Proust, it leaves the protoxide when very strongly ignited; and, according to Rothoff (*Schw.* 22, 329), 100 parts of sesquioxide of cobalt, heated to redness, give off from 9·5 to 9·9 parts of oxygen, and leave a residue of protoxide. [For the other decomposition, *vid. Hydrated Cobaltic Oxide.*)

	Calculation, according to Rothoff.			Winkelblech (1).	Proust.
2Co	59	71·08	70·94	79	to 80
3O	24	28·92	29·05	21	,, 20
Co^2O^3	83	100·00	99·99	100	,, 100

Combinations.—a. With Water.—Hydrated Cobaltic Oxide, or Cobaltic Hydrate.—1. Formed by saturating water in which hydrate or carbonate of cobalt oxide is diffused, with chlorine gas, then washing and drying. (Proust, Winkelblech.) The same compound may likewise be formed by boiling recently precipitated cobalt-hydrate with chloride of lime. (Böttger)—Bromine-water likewise converts the protoxide of cobalt into sesquioxide and bromide of cobalt, the latter dissolving. (Balard.)—2. By precipitating nitrate of cobaltous oxide with chloride of lime (Hess), or with chloride of soda mixed with caustic potash. If the potash were not added, nitrate of cobaltic oxide would remain in solution; this was mistaken by Dingler for cobaltate of soda,—but, when treated with potash, it yields a a precipitate of cobaltic oxide without any evolution of oxygen. To remove the chlorine completely, it is necessary to boil the precipitate with strong caustic of potash; otherwise, it will still emit an odour of chlorine when treated with acids. (Winkelblech.)—3. By exposing a salt of cobaltous oxide, supersaturated with ammonia, to the air, till it is converted into a brown liquid, and then precipitating by potash. (Winkelblech.)—When any cobalt-salt is exposed to the action of a voltaic battery of at least 100 pair of large plates, cobaltic oxide is deposited on the positive pole. (Fischer, *Kastn Arch.* 16, 218.)—The liquid should be well boiled before the precipitate is collected on a filter, otherwise it will adhere closely to the paper. (Winkelblech.)

Brownish-black, densely-aggregated mass, having a conchoidal fracture, and yielding a dark brown powder.

			Winkelblech. (2)	Winkelblech. (3)	Hess. (2)
2Co	59	53·64	53·83	53·93	81·7
3O	24	21·82	21·62	21·46	
3HO	27	24·54	24·26	24·61	18·3
Co^2O^3,3HO	110	100·00	99·71	100·00	100·0

The hydrate, in the analyses by Hess and Winkelblech, was previously finely pounded and dried over oil of vitriol in a receiver not exhausted of air; Hess kept it there for a week; according to his analyses, the hydrate $=Co^2O^3+2HO$.

The hydrate when heated, first gives off water, then oxygen gas and water together, and leaves Co^3O^4, which does not part with the remainder of the water till it has been kept at a red heat for some time. (Winkelblech.) It dissolves in sulphurous or hyponitric acid, with formation of sulphate or nitrate of cobaltous oxide. Ammonia dissolves it only on the addition of a piece of tin: the solution is red. In hot sulphuric or nitric acid it dissolves with evolution of oxygen, being converted into protoxide, and in hydrochloric acid with evolution of chlorine gas. (Proust.) In cold phosphoric, sulphuric, nitric, or hydrochloric acid, it dissolves at first without decomposition; but on exposure to light, or on the application of heat, oxygen or chlorine gas is evolved, and a salt of cobaltous oxide formed. (Winkelblech.)—Racemic, tartaric, and citric acid dissolve the hydrate, reducing it completely to the state of protoxide; hot aqueous oxalic acid forms oxalate of cobaltous oxide, and gives off carbonic acid. —The hydrate, if heated while yet moist with a solution of oxalate of ammonia, dissolves with evolution of ammonia, and forms a green solution of cobaltoso-cobaltic oxalate. (Winkelblech.) Aqueous ammonia exerts no decomposing action, even with the aid of heat. (Proust, Winkelblech.)

b. Cobaltic Salts.—Cold phosphoric, sulphuric, nitric, and hydrochloric acid dissolve the hydrated sesquioxide without decomposition at first, but the resulting salts are afterwards converted into salts of the protoxide. (*vid. sup.*) A cobaltous salt containing a small quantity of cobaltic salt, has a darker colour than that which properly belongs to it. —The most permanent of the cobaltic salts is the acetate; the hydrated oxide, while yet moist, dissolves in acetic acid slowly but completely. The intensely brown solution forms a brown precipitate with potash, carbonate of potash, or carbonate of ammonia; also with ammonia, which, however, does not precipitate all the cobalt. With hydrosulphuric acid and hydrosulphate of ammonia, it gives a black precipitate; with alkaline phosphates or arseniates, a brown precipitate; with ferrocyanide of potassium, a dark red precipitate, which, if the precipitant is in excess, gives up cyanogen to it, and converts it into ferricyanide of potassium, and is itself converted into green ferrocyanide of cobalt. Iodide of sodium colours the solution reddish-yellow; alkaline oxalates colour it yellow after a while, in consequence of the formation of cobaltoso-cobaltic oxalate. (Winkelblech.)

D. *Cobaltic Acid?* CoO^3.

The observations which appear to indicate the existence of this compound, will be found under the head of *cobalto-nitrate of ammonia.* (P. 342.)

Cobalt and Carbon.

Carbonate of Cobalt-oxide, or Cobalt-carbonate.—*Quintobasic.* —Formed by precipitating a cobalt-salt, at a boiling heat, with excess of monocarbonate or bicarbonate of potash.—Peach-blossomed-coloured *precipitate.*—The salt examined by Winkelblech was obtained with mono-

carbonate of potash; that of Setterberg (*Pogg.* 19, 55), the composition of which was given under (1), was precipitated by bicarbonate of potash, the liquid being kept constantly boiling; that given under (2), by adding protochloride of cobalt, in successive portions, to the boiling solution of bicarbonate of potash; that under (3), by precipitation at a temperature below the boiling point; the last-mentioned precipitate always gives up a small quantity of cobalt to warm water with which it is washed.—The composition corresponds with that of the zinc-salt, even in the quantity of water. When cobalt-salts are boiled with carbonate of soda in very large excess, the precipitate turns blue.

			Winkelblech.	Setterberg.		
				(1)	(2)	(3)
5CoO	187·5	70·10	70·11	70·06	68·76	68·91
$2CO^2$	44·0	16·45	16·12	16·45	18·76	19·06
4HO	36·0	13·45	13·51	13·49	12·48	12·03
$5CoO,2CO^2+4Aq.$	267·5	100·00	99·74	100·00	100·00	100·00

Insoluble in water; soluble in aqueous carbonate of ammonia, potash, or soda.

When cobalt-salts are precipitated in the cold by bicarbonate of potash, a rose-coloured, sparingly soluble precipitate is formed, which contains potash, and, by boiling with water, is converted into the salt just described. (Winkelblech.)

Cobalt and Boron.

Borate of Cobalt-oxide, or Cobalt-borate.—Formed by precipitating a cobalt-salt with borax.—Reddish-white powder, which is scarcely soluble in water, and fuses to a dark blue glass when heated.

Cobalt and Phosphorus.

A. Phosphide of Cobalt.—*a. With a very large excess of Cobalt.*—1. Formed by throwing pieces of phosphorus on red-hot cobalt.—2. By igniting 1 part of cobalt with 1 part of glacial phosphoric acid, and $\frac{1}{10}$ of charcoal powder. (Pelletier.)—3. By exposing a mixture of 70 pts. metallic or oxidized cobalt, 100 bone-ash, 50 pounded quartz, and 10 charcoal, to the heat of a blast-furnace for an hour. (Berthier.)—The compound, when prepared by (1) or (2), has the metallic lustre and a bluish-white colour; it is brittle, of acicular structure, more easily fusible than cobalt, contains 94 per cent. of cobalt and 6 per cent. of phosphorus, becomes dull on exposure to the air, and burns to a dark blue glass when heated. (Pelletier.)—By (3), of a shining white colour, very fusible, non-magnetic, and often has needle-shaped crystals in its cavities. (Berthier.)

b. Triphosphide.—1. Phosphuretted hydrogen gas converts heated chloride of cobalt into a grey substance, insoluble in strong hydrochloric acid, but easily soluble in nitric acid.—2. Triphosphate of cobalt-oxide, as obtained by precipitating the protochloride with diphosphate of soda, is easily decomposed by ignition in a stream of hydrogen, nothing but water being given off, and triphosphide of cobalt being left in the form of a

to one atom of acid. (H. Rose.) They dissolve in excess of phosphoric acid, forming a deep red solution; in ammonia, with first a yellowish and afterwards a brownish colour, and slightly in hydrochlorate or nitrate of ammonia.

E. PYROPHOSPHATE OF COBALT-OXIDE, or COBALT-PYROPHOSPHATE.—The precipitate which cobalt-salts form with dipyrophosphate of soda, is re-dissolved by an excess of the re-agent. (Stromeyer.)

¶ F. METAPHOSPHATE OF COBALT-OXIDE, or COBALT-METAPHOSPHATE.—Formed by adding a solution of cobalt-sulphate to an excess of dilute phosphoric acid, evaporating to dryness, and heating the residue in a platinum capsule above 316°; it then separates in the form of a beautiful rose-coloured powder, insoluble in water and dilute acid, but soluble in strong sulphuric acid.

					Maddrell.
CoO	37·5	....	34·43	.....	34·79
PO^5	71·4	....	65·57	.....	65·21
CoO,PO^5	108·9	....	100·00	.....	100·00

(Maddrell, *Ann. Pharm.* 58, 61.) ¶

COBALT AND SULPHUR.

A. PROTOSULPHIDE OF COBALT.—1. Formed by throwing sulphur on the metal heated to redness in a retort, the combination being attended with fusion and combustion. (Proust.)—2. By igniting the hydrated compound in a close vessel. (Proust.)—3. By heating protoxide of cobalt with sulphur. (Proust.)—4. Anhydrous sulphate of cobalt-oxide, heated to whiteness in a crucible lined with charcoal, leaves half its own weight of sulphide of cobalt. (Berthier.)—By (1): grey, with metallic lustre; laminar; dissolves easily in acids, with evolution of sulphuretted hydrogen (Proust); according to (4): grey, with granular fracture; magnetic (Berthier).

					Proust (1).
Co	29·5	....	64·84	.....	71·5
S	16·0	....	35·16	.....	28·5
CoS	45·5	....	100·00	.....	100·0

Hydrated Protosulphide of Cobalt, or Hydrosulphate of Cobalt-oxide.—Formed by precipitating acetate of cobalt-oxide with sulphuretted hydrogen, or any cobalt-salt with an alkaline hydrosulphate, or by bringing the hydrate or carbonate of cobalt-oxide in contact with sulphuretted hydrogen water. (Proust.) Black powder. When heated, it gives off a large quantity of water and sulphurous acid [?], and is converted into dry sulphide of cobalt. (Proust.) When exposed to the air in the moist state, it slowly oxidizes, and forms sulphate of cobalt-oxide. Dissolves, with evolution of hydrogen, in mineral acids when tolerably concentrated, very sparingly in cold dilute acids, and scarcely at all in dilute acetic acid. (Wackenroder.) Dissolves, while yet moist, in aqueous sulphurous acid. From sulphate of cadmic oxide, acetate of lead-oxide, hydrochlorate of ferric oxide, nitrate of nickel-oxide, sulphate of cupric oxide, and nitrate of silver-oxide, it precipitates the metals in the form of sulphides. (Anthon.)

B. Oxysulphide of Cobalt.—Formed by passing hydrogen gas over red-hot sulphate of cobalt-oxide. The decomposition goes on quickly, with formation of sulphurous acid and water. 100 pts. of the dry cobalt-salt yielding 50·02 parts of a dark grey powder aggregated in lumps. This substance contains 1 At. protoxide to 1 At. protosulphide of cobalt. It burns at a red heat, forming sulphurous acid and sesquioxide cobalt. To cold hydrochloric acid it gives up merely the cobalt-oxide already contained in it; but on the application of heat, sulphuretted hydrogen is likewise evolved. (Arfvedson, *Pogg.* 1, 64.) (Does not the protosulphide of cobalt, prepared by Berthier according to method (4), likewise belong to this head?)

C. Sesquisulphide of Cobalt.—Found in the form of *Cobalt-pyrites*. —*Preparation.*—1. By strongly igniting the protoxide or sesquioxide with sulphur, and exhausting the residue with water.—2. By heating the sesquioxide in hydrogen gas to a temperature somewhat below redness. (Berzelius.)—3. By passing sulphuretted hydrogen over red-hot oxysulphide of cobalt. 100 parts yield 117. (Arfvedson.)

Cobalt-pyrites forms regular octohedrons and cubo-octohedrons, of specific gravity 4·9 to 5·0. They are harder than Apatite, of a colour between tin-white and light steel-grey, and yield a blackish-grey powder. Artificial sulphide of cobalt (1) is graphitic and crystalline (Berzelius, Fellenberg, *Pogg.* 50, 73); (2) is dark grey (Berzelius). The native sulphide gives off sulphurous acid before the blowpipe, and fuses in the inner flame to a grey magnetic bead, exhibiting a bronze-yellow colour in the interior; after roasting, it imparts a blue colour to borax and microcosmic salt. Dissolves in nitric acid, with separation of sulphur. Sulphide of cobalt [the protosulphide or the sesquisulphide?] does not decompose vapour of water at a red-heat, even so much as sulphide of nickel. (Regnault.) Sesquisulphide of cobalt (1), heated in a stream of chlorine gas, yields chloride of sulphur and 122·9 per cent. of residual chloride of cobalt. (Fellenberg.) Chlorine does not act upon it in the cold, and but very slowly when aided by heat. (H. Rose, *Pogg.* 42, 540.)

					Fellenberg. (1.)		Wernekink. Miser.
2Co	59		55·14		55·45		53·35
3S	48		44·86		44·55		42·25
Fe							2·30
Cu							0·97
	107		100·00		100·00		98·87

D. Bisulphide of Cobalt.—1. Protoxide of cobalt is prepared by rapidly igniting the recently precipitated carbonate in a crucible, then mixed with three times its weight of sulphur, and the mixture slowly heated in a glass tube to a temperature a little below redness. If the mass is not quite black, it must be again mixed with sulphur and ignited. —2. By passing sulphuretted hydrogen over sesquioxide of cobalt at a temperature much below redness, and boiling the blackish-grey mass with hydrochloric acid. [Is this blackish-grey mass sesquisulphide of cobalt, or a mixture of the proto- and bisulphides?] Black powder, destitute of lustre. At a red heat, it gives off sulphur, and leaves a grey sulphide of cobalt. Not attacked by alkalis or by acids, excepting nitric acid and aqua regia. The sulphide prepared by (2), when exposed in the washed, moist state to the air, is partly converted into sulphuric acid and cobalt-sulphate. (Setterberg, *Pogg.* 7, 40.)

$i : u$ or $u' = 99° 45'$; $u : u' = 82° 20'$; $i : a = 152° 45'$; $i : \beta = 124°$; $i : d = 135° 55'$; $i : f = 118° 53'$. (Brooke.) The crystals have a faintly astringent, slightly bitter, and metallic taste, and when heated, give off water, without fusing, and become opaque and rose-coloured: they do not part with their acid, even at a red heat. (Proust.) They dissolve in 24 parts of cold water, but not in alcohol. Glacial acetic acid precipitates the salt completely from its aqueous solution, so that not a trace of cobalt remains in the liquid. (Persoz.) Marks made on paper with the solution, turn red when the paper is warmed. (Proust.)

	Anhydrous.				Rothoff.
CoO	37·5	....	48·39	....	47·89
SO^3	40·0	....	51·61	....	52·11
CoO, SO^3	77·5	....	100·00	....	100·00

	Crystallized.				Bucholz.		Mitscherlich.		Proust.
CoO	37·5	....	26·69	....	30 }	....	37·3	....	58
SO^3	40·0	....	28·47	....	26 }				
7HO	63·0	....	44·84	....	44	....	42·7	....	42
	140·5	....	100·00	....	100		100·0	....	100

When *native Cobalt-vitriol* from Bieber is freed by solution in water and filtration, from admixed arseniate of manganous oxide, the quantity of which is much below 1 per cent., the crystals obtained from the filtrate exhibit, according to Winkelblech, the following composition :

					Winkelblech.
1MgO	20·0	....	3·67	....	3·87
3CoO	112·5	....	20·66	....	19·91
$4SO^3$	160·0	....	29·39	....	29·05
28HO	252·0	....	46·28	....	46·83
	544·5	....	100·00	....	99·66

I. Sulphocarbonate of Cobalt.—Aqueous sulphocarbonate of calcium forms with cobalt-salts, a mixture which has a deep olive-green colour by transmitted, and black by reflected light: after 24 hours, it deposits black flakes, the liquid retaining a dark-brown colour.

Cobalt and Selenium.

A. Selenide of Cobalt.—Heated cobalt combines with selenium, forming a grey mass, which exhibits metallic lustre and crystalline structure, and fuses at a red heat : the combination is attended with ignition. (Berzelius.)

B. Selenite of Cobalt-oxide, or Cobalt-selenite.—*a. Monoselenite.*—Rose-coloured powder, insoluble in water. (Berzelius.)—*b. Biselenite.* Remains, on evaporating the aqueous solution, in the form of a transparent purple-red gum. (Berzelius.)

C. Cobalt-seleniate.—Identical in crystalline form with the sulphate. (Mitscherlich.)

Cobalt and Iodine.

A. Iodide of Cobalt.—CoI.—Pulverized cobalt and iodine heated together in a glass tube, unite and form a greyish-green mass which has no metallic lustre, fuses when heated, but does not sublime. (Erdmann, *J. pr. Chem.* 7, 354.)—By evaporating the aqueous solution, a dark green deliquescent mass is obtained. (Erdmann, Rammelsberg.)

Aqueous Iodide of Cobalt, or *Hydriodate of Cobalt-oxide.*—1. When cobalt reduced by hydrogen is placed in contact with iodine and water, the temperature of the liquid rises to the boiling point and a red solution is formed.—2. Dry iodide of cobalt forms with a small quantity of water a green solution (Erdmann), or brown (Rammelsberg); with a larger quantity of water, it forms a red solution.—Iodide of cobalt is soluble in alcohol. (Erdmann.)

B. *Oxy-iodide of Cobalt?*—CoO,CoI.—Ammonia, added to a dilute solution of iodide of cobalt, colours the liquid brown, and throws down a blue precipitate which turns green by oxidation during washing and drying. (Rammelsberg, *Pogg.* 48, 155.)

C. Iodate of Cobalt-oxide, or Cobalt-iodate.—The solution of recently precipitated carbonate of cobalt-oxide in aqueous iodic acid yields, both by cooling and by evaporation of the mother-liquid, violet-red crystalline crusts, which give off 5·5 per cent. of water at 200°, and, on subsequent ignition in a retort, are resolved into iodine vapour, oxygen gas, and black cobaltoso-cobaltic oxide, Co^3O^4, which still retains the crystalline form of the salt. They dissolve in 148 parts of water at 15°, and in 90 parts of boiling-water. (Rammelsberg, *Pogg.* 44, 561.)

	Anhydrous.		Rammelsberg.
CoO	37·5	18·43	18·35
IO^5	166·0	81·57	81·65
CoO,IO^5	203·5	100·00	100·00

	Crystallized.		Rammelsberg.
CoO	37·5	17·65	
IO^5	166·0	78·12	
HO	9·0	4·23	5·5
CO,Io^5 + Aq.	212·5	100·00	

Cobalt and Bromine.

A. Bromide of Cobalt.—1. Cobalt at a dull red heat takes up vapour of bromine, forming a green compound which fuses and is partially decomposed at a higher temperature. (Berthemot, *Ann. Chim. Phys.* 44, 391.)—2. The crystals of the hydrated bromide leave a bluish-green residue when heated. (Rammelsberg, *Pogg.* 55, 244.)

			Berthemot.
Co	29·5	27·34	27·43
Br	78·4	72·66	72·57
CoBr	107·9	100·00	100·00

Hydrated Bromide of Cobalt, or *Hydrobromate of Cobalt-oxide.*—Bromide of cobalt deliquesces rapidly in the air, forming a red liquid; the same solution is obtained by heating cobalt with bromine and water. The solution turns red on evaporation, leaving the green anhydrous compound as a residue. Ammonia added to the solution throws down a precipitate which is soluble in excess. (Berthemot.) When the solution is evaporated over oil of vitriol, red crystals are obtained which soon effloresce in the dry air of the receiver, but deliquesce when exposed to the atmosphere in its ordinary state. (Rammelsberg.)

B. Bromate of Cobalt-oxide, or Cobalt-bromate.—By precipitating sulphate of cobalt-oxide with bromate of baryta, and evaporating the filtrate over oil of vitriol, transparent regular octohedrons are obtained, having a hyacinth-red colour. They are isomorphous with the bromates of magnesia, zinc-oxide, and nickel-oxide. When heated, they are resolved into bromine vapour, oxygen gas, and sesquioxide of cobalt. They dissolve in 2·2 parts of cold water; and the solution evaporated at a gentle heat, gives off bromine vapour and deposits sesquioxide of cobalt. (Rammelsberg, *Pogg.* 55, 71.)

Anhydrous.			*Crystallized.*			Rammelsberg.
CoO	37·5	24·06	CoO	37·5	17·86	18·09
BrO^5	118·4	75·94	BrO^5	118·4	56·41	
			6HO	54·0	25·73	
CoO,BrO^5	115·9	100·00	+6Aq.	209·9	100·00	

Cobalt and Chlorine.

A. Chloride of Cobalt.—1. Heated cobalt powder takes fire in chlorine gas. (H. Davy.)—Finely divided cobalt takes fire in a stream of chlorine gas and produces blue crystalline scales. (H. Rose, *Pogg.* 24, 157.)—Chloride of cobalt is likewise obtained by heating the sulphide in a stream of chlorine. (Fellenberg.)—2. By evaporating the aqueous solution of chloride of cobalt to dryness, till the red colour of the liquid changes to greenish-blue.—The chloride thus obtained is a blue, loosely coherent mass, which does not turn red on cooling, but only on exposure to the air, the change being then due to absorption of water. When strongly ignited in a retort (Proust, Bucholz), or in a tube through which chlorine is passed (Fellenberg), it sublimes after fusing (Proust), or without fusing (Fellenberg) in soft, loose, crystalline spangles, which are slippery to the touch, and flax-blossom-coloured, according to Proust, blue according to Bucholz, and bluish-green according to Fellenberg.—Chloride of cobalt, when fused with phosphorus, yields chloride of phosphorus and phosphide of cobalt. (H. Rose, *Pogg.* 27, 117.) It is decomposed by phosphuretted hydrogen gas as easily as protochloride of copper. (H. Rose.) With oil of vitriol, even when cold, it gives off hydrochloric acid and chlorine [!] gas, and forms sulphate of cobalt-oxide. (A. Vogel.)—With aqueous hypochlorous acid, it evolves chlorine gas and yields a precipitate of hydrated sesquioxide of cobalt. (Balard.)

Co	29·5	45·45
Cl	35·4	54·55
CoCl	64·9	100·00

Hydrated and *Aqueous Chloride of Cobalt*, or *Hydrochlorate of Cobalt-oxide.*—Chloride of cobalt, even after sublimation, takes up water and turns red on exposure to the air, and is afterwards easily soluble in water; but the sublimed chloride, if not previously exposed to the air for a sufficient time, requires 12 hours or more to effect its complete solution. (Proust, Bucholz, Fellenberg.)—The same liquid is obtained by dissolving the pure hydrate or carbonate of cobalt-oxide in hydrochloric acid, or by dissolving the metal in hydrochloric acid or aqua-regia. —The red solution evaporated and cooled yields crystals belonging to the oblique prismatic system. *Fig.* 101, but without the *b*- or *c*-face or the face below it. $i : u$ or $u' = 109° 31'$; $i : t = 122° 20'$; $i : f$ behind $= 106° 20'$; $t : f = 131° 20'$; $u : d = 77° 20'$; $u : t = 128° 40'$. Cleavage distinct parallel to i, less distinct parallel to u. (Brooke, *Ann. Phil.* 23, 364.) The crystals are carmine-coloured and do not deliquesce in the air. According to Proust, who probably obtained them from an acid liquid, they are blue, and turn red in the air by absorption of water.

The carmine-coloured, aqueous solution of dry chloride of cobalt or of the crystals, turns blue when mixed with strong hydrochloric acid or oil of vitriol, the change taking place sooner the lower the temperature. The red colour is restored by addition of water, and partly also by cooling. The more dilute solution, if it contains free acid, likewise turns blue when evaporated by heat or in vacuo over oil of vitriol. (A. Vogel.) In a similar manner, marks made on paper with this solution, turn blue whenever the paper is heated, and resume their pale red colour on exposure to the air, doubtless by recovering their water. If the cobalt solution contains small quantities of ferric oxide or larger quantities of nickel-oxide, the blue colour is replaced by a bluish-green or a green tint. The liquid discovered by Waitz, called *Hellot's Sympathetic Ink*, is a solution of this kind; it may likewise be prepared by dissolving zaffre in hydrochloric acid, or by mixing cobalt-nitrate with sal-ammoniac or common salt.—Since anhydrous chloride of cobalt is blue, the blue tint appears to result from the formation of this compound: heat drives off the water, and strong acids abstract it. If the existence of hydrogen-acid salts be assumed, we must suppose that, when this change of colour takes place, the red hydrochlorate of cobalt-oxide is converted into blue chloride of cobalt; on the contrary supposition, the explanation will perhaps be, that the solution of hydrated chloride of cobalt in watery liquids is red, while that of the anhydrous chloride is blue.

Cobalt cannot be converted into a sesquichloride by treating it with excess of chlorine; but the recently prepared solution of the hydrated sesquioxide in cold hydrochloric acid contains this compound. (Winkelblech.)

¶ B. Chlorate of Cobalt-oxide.—$CoO,ClO^5 + 6Aq$.—Crystallizes in cubes combined with octohedrons. Decomposed by ignition into chlorine, oxygen, and a residue of oxide and chloride of cobalt. (Wächter, *Ann. Pharm.* 52, 233.) ¶

Cobalt and Fluorine.

A. Fluoride of Cobalt and Hydrofluate of Cobalt-oxide.—The solution of carbonate of cobalt-oxide in excess of aqueous hydrofluoric acid deposits on evaporation, as the free acid escapes, a rose-coloured, crystalline crust. (Gay-Lussac & Thénard.) The composition

of this deposit is CoF,2HO. It dissolves without decomposition in water containing hydrofluoric acid, also in small quantities of pure cold water, forming a saturated solution which again yields crystals on evaporation; but, on boiling with larger quantities of water, the crystalline crust is resolved into an acid salt which dissolves and the compound B.—Fluoride of cobalt unites with the fluorides of the alkali-metals, forming sparingly fusible, slightly coloured salts. (Berzelius.)

B. Oxyfluoride of Cobalt.—2(CoO,CoF) + HO.—Produced in the form of a pale red powder when fluoride of cobalt is boiled with water, or when aqueous hydrofluoric acid is digested with excess of cobalt-carbonate. (Berzelius, *Pogg.* 1, 26.)

Cobalt and Nitrogen.

A. Nitrate of Cobalt-oxide, or Cobalt-nitrate.—*a. Sexbasic.*—The blue precipitate produced by adding excess of ammonia to a well boiled solution of mononitrate of cobalt-oxide, the air being carefully excluded.—On the slightest access of air, the precipitate quickly assumes a grass-green colour, and gradually redissolves in the liquid; but the portion which remains undissolved, if washed by repeated agitation with thoroughly boiled water—access of air being prevented as much as possible—and then quickly dried between folds of bibulous paper, dries up to a grass-green powder. This powder when heated gives off water and acquires a darker colour; when dissolved in cold nitric or acetic acid, it leaves brown flakes which do not dissolve till the liquid is heated. It turns brown when boiled with caustic potash, which abstracts the nitric acid, but does not give rise to evolution of ammonia. Aqueous oxalic acid converts it into pale red oxalate of cobalt-oxide, but the greenish colour of the solution likewise indicates the formation of cobaltoso-cobaltic oxalate. The green precipitate, if immersed, while fresh, in water contained in a vessel exposed to the air, is gradually converted into yellow hydrate of cobaltoso-cobaltic oxide (p. 326), while the water takes up monobasic cobalt-nitrate and turns red.

	Green precipitate.				Winkelblech.
6CoO	225	....	69·44	.....	69·30
NO^5	54	....	16·67	.....	16·54
5HO	45	....	13·89	.....	14·16
6CoO, NO^5 + 5Aq.	324	....	100·00	.....	100·00

The blue precipitate must be regarded as the pure sexbasic salt; the green compound contains a small quantity of yellow cobaltoso-cobaltic hydrate; nevertheless it appears, from the quantity of carbonic acid which it evolves when heated with oxalic acid and a small quantity of water, that it only contains 0·502 per cent. more of oxygen than it should contain if it consisted wholly of a salt of the protoxide. (Winkelblech.)

b. Monobasic.—Formed by dissolving the metal, the protoxide, the hydrated protoxide, or the carbonate in dilute nitric acid.—The carmine-coloured solution yields red crystals on evaporation. They deliquesce in moist air, and contain 6 atoms of water. (Millon, *Compt. rend.* 14, 905.) They fuse below 100°, and at a higher temperature give off water and melt into a violet-red liquid, which afterwards becomes green and thickish, and is ultimately converted, with violent intumescence and evolution of nitrous fumes, into black sesquioxide of cobalt. Characters written on

paper with the solution of this salt, assume a peach-blossom colour whenever the paper is heated. (Proust.)

Anhydrous.			*Crystallized.*		
CoO	37·5	40·98	CoO	37·5	25·78
NO^5	54·0	59·02	NO^5	54·0	37·11
			6HO	54·0	37·11
CoO,NO^5	91·5	100·00	+ 6Aq.	145·5	100·00

Protoxide of cobalt neither dissolves nor suffers any alteration when immersed in aqueous *Ammonia* either warm or cold; but if an ammoniacal salt be added, and the air has access to the liquid, the oxide dissolves and forms a brown solution. (Winkelblech.)

B. Carbonate of Cobalt-oxide and Ammonia.—*Cobaltoso-ammonic Carbonate.*—Formed by dissolving carbonate of cobalt-oxide in aqueous carbonate of ammonia, or in pure ammonia, whereby the oxide is separated out; or by dissolving hydrated cobalt-oxide in carbonate of ammonia, whereupon ammonia is perhaps set free. Carmine-coloured liquid which is not rendered turbid by water, so long as it contains but a slight excess of ammonia. (Proust.) When exposed to the air, it deposits small crystals of cobalt carbonate.

The rose-coloured solution of *Metaphosphate of cobalt-oxide in Ammonia* yields no deposit on exposure to the air, even if it be evaporated to the consistence of a syrup. (Persoz, *Ann. Chim. Phys.* 56, 333.)

C. Cobalto-hyposulphate of Ammonia.—A concentrated solution of hyposulphate of cobalt-oxide, mixed with ammonia and heated, yields a green precipitate and a violet-red liquid from which red crystals are deposited in the cold. The mother-liquid becomes turbid when evaporated, from deposition of hydrated cobalt-oxide, and ultimately yields crystals of hyposulphate of ammonia.—Red rectangular prisms which soon turn brown and lose their lustre. With water they are resolved into a pale red solution—which, besides a small quantity of cobalt, contains ammonia and hyposulphate of ammonia—and green flakes, which contain cobalt and hyposulphuric acid but no ammonia, dissolve in cold hydrochloric acid with evolution of chlorine, and probably consist of basic hyposulphate of cobalt-oxide. (Rammelsberg, *Pogg.* 58, 296.)

	Crystallized.		Rammelsberg.
$5NH^3$	85	27·25	27·27
Co^2O^3	83	26·60	25·27
$2S^2O^5$	144	46·15	44·60
$3NH^3,Co^2O^3+2(NH^3,S^2O^5)$	312	100·00	97·14

D. Ammonio-sulphate of Cobalt-oxide.—Anhydrous sulphate of cobalt-oxide absorbs 66·48 per cent. of ammoniacal gas, with strong evolution of heat and considerable tumefaction, and forms with it a very pale reddish-white powder. At a moderate red heat, this substance melts, turns blue, gives off a large quantity of ammonia, and yields a small sublimate of sulphite of ammonia. It dissolves in water, forming a reddish solution, with separation of green flakes. (H. Rose, *Pogg.* 20, 152.)

			H. Rose.
$3NH^3$	51·0	39·69	39·93
CoO,SO^3	77·5	60·31	60·07
$3NH^3+CoO,SO^3$	128·5	100·00	100·00

E. Sulphate of Cobalt-oxide and Ammonia.—Red crystals= NH^4O,SO^3+CoO,SO^3+6Aq, isomorphous with those of sulphate of magnesia and ammonia. (Mitscherlich, comp. Proust, *N. Gehl.* 3, 411.)

F. Ammonio-iodide of Cobalt.—*Terbasic.*—Dry iodide of cobalt becomes strongly heated in a stream of ammoniacal gas, swelling up and absorbing 28·695 per cent. of the gas, and is converted into a reddish yellow powder. (Rammelsberg.)

			Rammelsberg.
$3NH^3$	51·0	24·70	22·30
CoI	155·3	75·30	77·70
$3NH^3$,CoI	206·5	100·00	100·00

b. Bibasic.—The concentrated solution of iodide of cobalt forms with ammonia a reddish-white, pulverulent precipitate, which dissolves when heated, leaving only a few dark green flakes, and forms a violet liquid; this solution assumes a deep red colour on cooling, and soon deposits small rose-coloured crystals, having the same composition as the reddish-white powder. The crystals, when heated, leave a residue of iodide of cobalt; and when this residue is dissolved in water, 19 per cent. of oxy-iodide of cobalt remains undissolved, and ammonia and water are set free. The water, which amounts to between 3 and 7 per cent. does not appear to be essential to the constitution of the compound; it does not, however, escape till the temperature is raised above 100°, and cannot therefore be removed without decomposition of the substance. The crystals, even when dried in the air, give off ammonia, turn brownish, and afterwards green. When the crystals are dissolved in water, ammonia is set free and oxy-iodide of cobalt separates in green flakes; the colourless liquid, which contains much iodine and a small quantity of cobalt, acquires a reddish colour by exposure to the air. (Rammelsberg, *Pogg.* 48, 155.)

	After deducting the water.		Rammelsberg.
$2NH^3$	34·0	17·94	
CoI	155·5	82·06	80·66
$2NH^3$,CoI	189·5	100·00	

G. Iodate of Cobalt-oxide and Ammonia.—The red-brown solution of cobalt-iodate in ammonia yields, on the addition of alcohol, a pale rose-coloured precipitate, which, when heated, first becomes yellowish-brown, then black, and gives off ammonia, iodine, oxygen gas, and water. The compound is likewise decomposed by water. (Rammelsberg, *Pogg.* 44, 561.)

H. Ammonio-bromide of Cobalt.—Anhydrous bromide of cobalt absorbs ammoniacal gas and is converted into a red powder, which turns brown after some time. This substance gives off its ammonia when heated. Water immediately resolves it into green flakes, which contain bromine even after washing, and a light brown ammoniacal liquid, which, when evaporated over oil of vitriol, leaves a brown, amorphous mass;

the latter dissolves in water, forming a red-brown solution, and leaves a residue of brown hydrated sesquioxide of cobalt. (Rammelsberg, *Pogg.* 55, 245.)

					Rammelsberg.
$3NH^3$	51·0	....	32·09	....	31·2
CoBr	107·9	....	67·91	....	68·8
$3NH^3$,CoBr	158·9	....	100·00	....	100·0

I. *Ammonio-sesquibromide of Cobalt?*—A concentrated solution of bromide of cobalt saturated with ammonia yields blue flakes and a red liquid; the former quickly turn green when exposed to the air; the latter turns brown and sometimes, though rarely, yields a few red, square tables. These crystals, when heated, give off ammonia and hydrobromate of ammonia, then bromine, and leave a green residue of bromide of cobalt. They dissolve in water, forming a red solution, which, soon after boiling, becomes turbid, gives off ammonia, and yields a brown precipitate of hydrated sesquioxide of cobalt; potash does not precipitate the hydrated sesquioxide till the liquid is boiled. The crystals are probably a compound of sesquibromide of cobalt with ammonia.—When the solution of bromide of cobalt supersaturated with ammonia and turned brown by exposure to the air—in which state it gives no precipitate with alcohol—is gently evaporated, it deposits brown hydrated sesquioxide of cobalt; and the filtrate, if left to evaporate over oil of vitriol, dries up to a brown mass, which may be freed by washing with alcohol from the admixed crystals of hydrobromate of ammonia. The brown residue dissolved in a small quantity of water and filtered from the reproduced hydrated sesquioxide, deposits, on the addition of alcohol, a brown powder which contains ammonia, and forms a dark-coloured solution in water; it contains 20·39 p. c. ammonia, 22·67 cobalt, 37·75 bromine, and a large quantity of water—probably $3Co^2O^3$, $2Co^2Br^3$, $15NH^3+20Aq$. (Rammelsberg.)

K. *Cobalto-bromate of Ammonia?*—Bromate of cobalt-oxide heated with ammonia forms a blue precipitate which turns green in the air, and a dark red solution which acquires a dark brown colour by exposure to the air, and when sufficiently concentrated and exposed to a low temperature, deposits red needles. If it be then evaporated, it becomes turbid and deposits brown hydrated sesquioxide; and if afterwards filtered, mixed with a small quantity of ammonia and evaporated over oil of vitriol, it deposits dark brown spherical aggregates of small crystals, which are apt to decompose and exhale bromine during drying. They deliquesce in the air with tolerable rapidity and form a brown mass; dissolve without turbidity in water; evolve chlorine [bromine?] when treated with hydrochloric acid, and ammonia when treated with potash, hydrated sesquioxide of cobalt being precipitated in the latter case.

	Crystallized.				Rammelsberg.
$7NH^3$	119·0	....	11·85	....	11·85
Co^2O^3	83·0	....	8·26	....	8·56
$6BrO^5$	694·4	....	69·14	....	67·96
12HO	108·0	....	10·75		
	1004·4	....	100·00		

According to this, the compound should be: $NH^3,Co^2O^3+6(NH^3,BrO^5)+12Aq$, or if cobaltic acid be supposed to be present instead of the sesqui-

oxide: $NH^3,2CO^2+6(NH^3,BrO^5)+12Aq$. Rammelsberg deduces from his analyses, the formula: $(4NH^3+Co^2O^3, 3BrO^5+9Aq)+2NH^3, BrO^5$.

L. Ammonio-chloride of Cobalt.—Dry chloride of cobalt very rapidly absorbs 52·43 per cent. of ammoniacal gas, the combination being attended with rise of temperature and intumescence; the product is a bulky powder of a very pale reddish-white colour. This substance when ignited gives off a large quantity of ammonia and a little sal-ammoniac, and leaves a blue mass only partially soluble in water. The unignited powder forms a red-brown solution in water, green protoxide of cobalt being separated. (H. Rose, *Pogg.* 20, 157.)

					H. Rose.
$2NH^3$	34·0		34·38		34·40
$CoCl$	64·9		65·62		65·60
$2NH^3,CoCl$	98·9		100·00		100·00

M. Fluoride of Cobalt and Ammonium.—Pale red crystalline granules, slightly soluble in water. (Berzelius.)

N. Nitrate of Cobalt-oxide and Ammonia.—Formed by mixing a solution of cobalt-nitrate [containing excess of acid ?] with ammonia. Rose-coloured cubes and funnel-shaped masses like those of common salt, permanent in the air, having a urinous taste, and deflagrating in a red-hot crucible, like nitrate of ammonia. (Thénard, *Scher. J.* 10, 426.)

O. Cobalto-nitrate of Ammonia.—A perfectly neutral solution of cobalt-nitrate yields, with ammonia, a blue precipitate which soon turns green. The liquid becomes brown in the air; and if it be shaken up with air for some time in a closed vessel, oxygen is absorbed, and the whole of the green precipitate ultimately dissolved. (According to Winkelblech, the precipitate is but partially redissolved.) The clear dark-brown solution thus obtained, deposits at a low temperature brown, transparent, four-sided prisms. If the cobalt-solution contains excess of nitric acid, it forms with ammonia a clear red mixture, which, when agitated with air, is converted into the same brown liquid.—An acid solution of cobalt-nitrate supersaturated with ammonia in a tube filled with oxygen gas and standing over mercury (whereby no turbidity is produced) and then agitated, absorbs 3·9 pts. (nearly ½ At.) of oxygen for every 37·5 pts. (1 At.) of protoxide of cobalt dissolved. This would indicate the formation of sesquioxide of cobalt, were it not that we may suppose that part of the cobalt remains in solution as protoxide, and that certain decompositions of the liquid, *e. g.* the evolution of nitrogen by potash, seem to denote a higher degree of oxidation.

The crystals dissolve without decomposition in aqueous ammonia, and form a brown solution; but in water they dissolve but partially, with evolution of nitrogen, and separation of brown hydrated sesquioxide of cobalt. When exposed to the air, they become dull and reddish, probably from loss of ammonia and absorption of carbonic acid.—The brown liquid obtained by supersaturating nitrate of cobalt-oxide with ammonia, and agitating with air, gives off nitrogen gas when heated, and assumes a red colour, but remains clear. (According to Hess, the liquid may be boiled without decomposition.)—When exposed to the open air, it is red from loss of ammonia and absorption of carbonic acid, and deposits hydrated sesquioxide of cobalt. With potash at ordinary tempe-

ratures, it slowly evolves nitrogen, and deposits brown hydrated sesquioxide. (According to Hess, it forms a dingy green precipitate with potash, not in the cold, but on the application of heat, and the decomposition takes place without evolution of gas. According to Winkelblech, also, no nitrogen is evolved in this reaction. The author introduced potash into a quantity of the brown liquid standing over mercury, and invariably obtained an evolution of gas.)—The liquid, when mixed with cold sulphuric or nitric acid, gives off oxygen, and assumes a pale red colour. (Gm.)

The sulphate and hydrochlorate of cobalt-oxide exhibit totally different reactions with ammonia.

Neutral *Sulphate of Cobalt-oxide* forms with ammonia a copious blue precipitate which soon turns green, and if agitated with air for some time, becomes brown, but does not dissolve; the supernatant liquid is red. —If the solution of the sulphate is previously supersaturated with sulphuric acid, it yields with ammonia a pale red mixture, which becomes pale brown on agitation, and, in the course of 24 hours, deposits a few brown transparent crystalline tables, the liquid itself assuming a pale red colour.

Neutral *Hydrochlorate of Cobalt-oxide* yields with ammonia a copious blue precipitate, which soon turns green, and if agitated with air assumes a brown colour, but does not dissolve: the supernatant liquid is pale red. —If the solution has been previously mixed with sal-ammoniac, the addition of ammoniac produces a clear, pale red mixture, which, when agitated with air in a close vessel, soon becomes light brown, then dark brown, and thereupon yields a brown precipitate, while the liquid resumes its red colour.

With *Sulphate of Cobalt-oxide and Potash*, ammonia produces first a blue, then a green, and lastly a brown precipitate, and a colourless liquid. (Gm.)

Cobalt and Potassium.

A. Cobaltite of Potash.—*a.* Protoxide of cobalt dissolves in fused hydrate of potash, forming a clear, blue liquid, which when heated for a somewhat longer time, becomes brown and solid, while the cobalt separates out in the form of sesquioxide. The blue liquid forms a blue mass on solidifying. (Gm.)

b. When a cobalt-solution is dropped into strong boiling potash-ley, the blue precipitate first changes into the red hydrate, and afterwards dissolves, forming a blue solution. This solution, when diluted with water, deposits the cobalt in the form of hydrated protoxide, and if the the air has access to it, in the form of sesquioxide (Proust); see also Völker (*Ann. Pharm.* 59, 34).

B. Carbonate of Cobalt-oxide and Potash.—*a.* Cobalt-oxide dissolves pretty freely in carbonate of potash, when heated with it before the blowpipe on platinum; the mass appears black when cold. (Berzelius.)—*b.* The hydrate and carbonate of cobalt-oxide, but not the ignited oxide, dissolve in strong carbonate of potash, forming a red solution, which is precipitated by dilution with water, but not by heat. (Proust, Gmelin.)

C. Sulphate of Cobalt-oxide and Potash.—Red crystals having the same form as those of sulphate of magnesia and ammonia. (Mitscherlich.) The crystals are somewhat less soluble in water than those of cobalt-sulphate. (Proust.)

Crystallized.	Mitscherlich's Calculation.		Proust.
KO	47·2	21·58	
CoO	37·5	17·15	
$2SO^3$	80·0	36·58	
6HO	54·0	24·69	26
$KO,SO^3 + CoO,SO^3 + 6Aq.$	218·7	100·00	

D. Fluoride of Cobalt and Potassium.—Pale red, granular crystals, slightly soluble in water. (Berzelius.)

Cobalt and Sodium.

A. Cobaltite of Soda.—Cobalt-oxide behaves with soda in the same manner as with potash.

B. Carbonate of Cobalt-oxide and Soda.—*a*. Carbonate of soda heated on platinum before the blowpipe with protoxide of cobalt, dissolves much less of that oxide than carbonate of potash; the mass, while in the fused state, appears reddish by transmitted light; on cooling it turns grey. (Berzelius.)—*b*. On supersaturating a cobalt-salt with strong carbonate of soda, the red precipitate redissolves and forms a red solution.

C. and D.—Cobalt-salts dissolve in fused *Borax* or *Microcosmic Salt*, forming a clear blue glass, the colour of which is so strong that it appears black if the quantity of cobalt is somewhat large.

¶ E. Metaphosphate of Cobalt-oxide and Soda.—Phosphoric acid prepared and purified by Gregory's method (II. 130), and still containing magnesia and soda, is mixed with solution of cobalt-sulphate, the liquid evaporated to a syrupy consistence, and the residue heated above 316°.—The salt thus obtained is of a fine rose-colour; it is insoluble in water and dilute acids, but dissolves in strong sulphuric acid.

			Maddrell.
6CoO	225·0	29·77	30·28
NaO	31·0	4·14	4·36
$7PO^5$	499·8	66·09	65·46
$6(CoO\ PO^5) + NaO,PO^5$	754·8	100·00	100·10

(Maddrell, *Ann. Pharm.* 61, 57.) ¶

Cobalt and Calcium.

Hypophosphite of Cobalt-oxide and Lime.—By boiling hypophosphite of lime with oxalate of cobalt-oxide in excess, and evaporating cooling the filtrate, red octohedrons are obtained which rapidly ·nesce. When heated in a retort, they evolve a mixture of hydrogen

and phosphuretted hydrogen, not inflammable at ordinary temperatures; and leave a residue, which is insoluble in hydrochloric acid, not even giving up its lime to that acid. (H. Rose, *Pogg.* 12, 295.)

Crystallized.					H. Rose.
2CaO	56·0	....	19·73	....	18·76
CoO	37·5	....	13·22	....	13·47
3PO	118·2	....	41·67	....	
8HO	72·0	....	25·38	....	
2(CaO,PO) + CoO,PO + 8Aq.	283·7	....	100·00		

Cobalt and Magnesium.

Cobaltite of Magnesia.—*a.* Magnesia ignited with cobalt-nitrate assumes a pale rose-colour. Minerals containing magnesia likewise exhibit a rose-colour when their powder is ignited with cobalt-nitrate, provided they do not contain alumina or a heavy metallic oxide. (Berzelius.)—*b.* When ammonia is added to a mixture of neutral hydrochlorate of cobalt-oxide and hydrochlorate of magnesia, a green precipitate is produced, which contains 10 per cent. of magnesia; does not turn brown during washing, but remains green; is insoluble in pure ammonia and carbonate of ammonia, but dissolves easily in sal-ammoniac, forming a dingy yellow solution, from which it is again precipitated by potash, and turns blackish-grey on ignition. (Berzelius, *Pogg.* 33, 126.)

Cobalt and Aluminum.

Aluminate of Cobalt-oxide.—When alumina, or a body containing alumina, or the precipitate obtained on adding an alkali to a mixture of alumina, as free as possible from iron, with a cobalt-salt, is ignited with cobalt-nitrate, a bright blue compound is produced. *Leithner's Blue,* which, after ultramarine, is the best and most permanent colour for oil-painting, and is likewise used for colouring on porcelain, is of this composition. *Thénard's Blue,* obtained by igniting hydrate of alumina with phosphate or arseniate of cobalt-oxide, likewise belongs to this head. ¶ According to Louyet (*Instit.* 1849, 206), a mixture of hydrate of alumina and hydrated cobalt-oxide does not assume a blue colour till it is heated to the melting point of glass, a red heat merely rendering it black or grey; whereas a mixture of hydrate of alumina with phosphate or arseniate of cobalt-oxide, becomes blue when heated merely to redness. ¶

Cobalt and Silicium.

A. Silicate of Cobalt-oxide.—The aqueous solution of soluble glass produces with cobalt-salts a beautiful blue precipitate, which becomes very pale on drying. (Fuchs, *Kastn. Arch.* 5, 400.) The solution of quadrosilicate of soda gives no precipitate with cobalt-salts. (Walckner.)

B. Hydrated Fluoride of Silicium and Cobalt, or Hydrofluate of Silica and Cobalt-oxide.—Obtained by dissolving carbonate of

cobalt-oxide in hydrofluosilicic acid. Pale red rhombohedrons and six-sided prisms=$CoF, SiF^2+7Aq.$, easily soluble in water. (Berzelius.)

C. Cobalt-glass.—Cobalt-oxide imparts to glass fluxes a deep and pure blue colour.—By fusing roasted cobalt-ores with quartz-sand and potash, a dark blue glass is obtained, which when pulverized forms *Smalt.*

Cobalt and Tungsten.

A. Tungstate of Cobalt-oxide.—*a. Monotungstate.*—Alkaline monotungstates form with neutral cobalt salts a precipitate, which assumes a violet colour after washing and drying—becomes greenish-blue, and gives off water at a red heat—and at a higher temperature, cakes together slightly, and becomes bluish-black. It is insoluble in water and in cold nitric acid, imperfectly soluble in oxalic acid, but perfectly soluble in heated phosphoric or acetic acid. (Anthon.)

	Ignited.				Anthon.
CoO	37·5	....	23·81	....	23·6
WO^3	120·0	....	76·19	....	76·4
CoO,WO^3	157·5	....	100·00	....	100·0

	Dried in the air.				Anthon.
CoO	37·5	....	21·37	....	21
WO^3	120·0	....	68·38	....	68
2HO	18·0	....	10·25	....	11
+2Aq.	175·5	....	100·00	....	100

b. Bitungstate.—By precipitating with an alkaline bitungstate. Red-brown, insoluble in water, imperfectly soluble in oxalic acid, but perfectly soluble in phosphoric or acetic acid, and in ammonia. (Anthon, *J. pr. Chem.* 9, 344.)

					Anthon.
CoO	37·5	....	13·52	....	14·28
$2WO^3$	240·0	....	86·48	....	85·72
$CoO,2WO^3$	277·5	....	100·00	....	100·00

					Anthon.
CoO	37·5	....	12·31	....	13
$2WO^3$	240·0	....	78·82	....	78
3HO	27·0	....	8·87	....	9
+3Aq.	304·5	....	100·00	....	100

B. Sulphotungstate of Cobalt.—CoS,WS^3.—The aqueous mixture of sulphotungstate of potassium and a cobalt-salt, is dark brown, and in the course of 24 hours yields a black precipitate. (Berzelius.)

Cobalt and Molybdenum.

A. Molybdate of Cobalt-oxide.—Dirty yellow precipitate, which becomes red when dry, and is decomposed by alkalis and by the stronger acids. (Berzelius.)

B. SULPHOMOLYBDATE OF COBALT.—Black-brown precipitate, which dissolves in the aqueous potassium-compound, imparting a black colour to the liquid. (Berzelius.)

C. PERSULPHOMOLYBDATE OF COBALT.—Dark red-brown precipitate (Berzelius.)

COBALT AND VANADIUM.

VANADIATE OF COBALT-OXIDE.—*Monovanadiate.*—Reddish straw-yellow, insoluble in water.—*b. Acid Vanadiate.*—Soluble in water, from which alcohol precipitates it in the form of a rusty yellow powder. (Berzelius.)

COBALT AND CHROMIUM.

CHROMATE OF COBALT-OXIDE.—Monochromate of potash forms, with cobalt-salts, a light red-brown precipitate, probably consisting of a basic salt, inasmuch as the liquid retains its orange-yellow colour. (Gm.)

COBALT AND MANGANESE.

Hypermanganate of potash does not precipitate cobalt-salts. (Fromherz.)

PEROXIDE OF MANGANESE WITH PROTOXIDE OF COBALT.—*Black Earthy Cobalt.*—Amorphous, very friable; has an earthy and plano-conchoidal fracture. Sp. gr. 2·22; colour brown-black. When heated, it gives off water and oxygen gas, sometimes also arsenious acid. Does not fuse before the blowpipe; colours borax blue: with carbonate of soda on platinum, it yields mineral chameleon; and on charcoal in the inner flame, a white, slightly magnetic metal. Dissolves in cold, strong, hydrochloric acid, forming a brown solution, which turns blue when heated, and becomes red on cooling: the act of solution is attended with copious evolution of chlorine. According to Rammelsberg (*Pogg.* 54, 551), the ore from Saalfeld should be regarded as $(CoO; CuO),2MnO^2+4Aq$; the quantity of manganese is, however, much too small to agree with this formula.

	At.	*Black Earthy Cobalt.*		Rammelsberg. Saalfeld.
KO				0·37
BaO				0·50
CoO	5	187·5	19·30	19·45
CuO	1	40·0	4·12	4·35
MnO	12	432·0	44·46	40·05
O	12	96·0	9·88	9·47
HO	24	216·0	22·24	21·24
Fe^2O^3				4·55
		971·5	100·00	99·99

Yellow Earthy Cobalt is a dense or earthy mixture of the hydrated arseniates of lime, cobalt-oxide, and ferric oxide, and often contains a small quantity of antimony.

Cobalt and Arsenic.

A. Arsenide of Cobalt.—*a.* A mixture of 2 parts of cobalt and 3 of pounded arsenic, yields, when heated, a blackish-grey, porous compound, whose formation is attended with the emission of a red light. (Gehlen.)

b. At the blue-colour works at Modum, the two following alloys are formed: *α.* Obliquely truncated rhombic needles, united in tufts. *β.* Large tables having the metallic lustre. (Th. Scheerer & Francis, *Pogg.* 50, 513.) The composition of both these alloys is nearly 5(Fe; Co; Cu)As.

	At.						Scheerer & Francis.
Fe	5	....	135·0	....	10·21	....	10·05
Co	25	....	737·5	....	55·76	....	53·71
Cu		....		....		....	0·86
As	6	....	450·0	....	34·03	....	36·02
S		....		....		....	0·16
			1322·5	....	100·0	....	100·80

	At.						Scheerer & Francis.
Fe	10	....	270	....	24·66	....	23·15
Co	12	....	354	....	32·32	....	31·35
Cu	3	....	96	....	8·77	....	8·90
As	5	....	375	....	34·25	....	35·20
S		....		....		....	0·50
			1095	....	100·00	....	99·10

c. Tin-white Cobalt, Cobaltine, Smaltine, Speiskobold.—Belongs to the regular system. *Fig.* 1, 2, 3, 4, and 5. Sp. gr. 6·5; harder than apatite. Colour tin-white, inclining to steel-grey; powder greyish-black. When heated to redness in a retort, it yields a sublimate of arsenic, and a non-magnetic compound containing less arsenic. Heated upon charcoal, it gives off a copious arsenical fume, and fuses into a white, brittle, metallic globule, which, after being roasted, imparts a blue colour to glass. (Berzelius.) Hot nitric acid dissolves it, with separation of arsenious acid.

			Cobaltine.				Stromeyer. *a.*
	At.						
Fe	2	....	54·0	....	3·99	....	3·42
Co	11	....	324·5	....	23·98	....	20·31
Ni		....		....		....	
Cu		....		....		....	0·16
As	13	....	975·0	....	72·03	....	74·21
Bi		....		....		....	
S		....		....		....	0·88
			1353·5	....	100·00	....	98·98

	At.						Hofmann. *b.*
Fe	7	....	189·0	....	11·42	....	11·71
Co	8	....	236·0	....	14·26	....	13·95
Ni	1	....	29·5	....	1·79	....	1·79
Cu		....		....		....	1·39
As	16	....	1200·0	....	72·53	....	70·37
Bi		....		....		....	0·01
S		....		....		....	0·66
			1654·5	....	100·00	....	99·88

	At.						Varrentrapp. c.
Fe	2	....	54·0	....	4·72	....	4·95
Co	9	....	265·5	....	23·20	....	23·44
As	11	....	825·0	....	72·08	....	69·46
S		....		....		....	0·90
			1144·5	....	100·00	....	98·75

a. is crystallized cobaltine, from Riechelsdorf;—*b.* massive cobaltine, from Schneeberg;—*c.* massive cobaltine, from Tunaberg: sp. gr. 7·131 [?]. According to the preceding analyses, the general formula of cobaltine is: (Co; Fe; Ni)As.

¶ A variety of cobaltine, from Riechelsdorf, remarkable for the large proportion of nickel which it contains, has been examined by Sartorius (*Ann. Pharm.* 66, 278): its composition in 100 parts is: 9·17Co + 14·06Ni + 1·42Fe + 73·53As = 98·18. ¶

d. Tesseral Pyrites, from Skütternd.—Co^2As^3.—Cubes and octohedrons with the faces of the cube, dodecahedron, and leucitohedron; sp. gr. 6·78. Tin-white. When roasted in an open glass tube, it yields a copious sublimate of metallic arsenic and arsenious acid. (Th. Scheerer, *Pogg.* 42, 553; Wöhler, 43, 592.)

Tesseral Pyrites.					Scheerer.		Wöhler. *Crystallized.*		*Massive.*
Fe		....		....	1·51	....	1·3	....	1·4
2Co	59	....	20·77	....	20·01	....	18·5	....	19·5
Cu		....		....	trace	....		....	
3As	225	....	79·23	....	77·84	....	79·2	....	79·0
S		....		....	0·69	....		....	
	284	....	100·00	....	100·05	....	99·0	....	99·9

B. Arsenite of Cobalt-oxide, or Cobalt-arsenite.—The inner portion of *Cobalt-bloom* sometimes, though rarely, consists of this mineral. (Proust.) The arsenite formed by mixing a dissolved cobalt-salt with arsenite of potash has the form of a rose-coloured precipitate, which becomes dark-coloured and horny when dry. When heated in a glass vessel it gives off arsenious acid and colours the glass blue; heated potash resolves it into cobalt-oxide and a blue liquid, which deposits the oxide on the addition of water. Dissolves in nitric acid, with evolution of nitrous gas; also in hydrochloric acid, and in ammonia, in the latter of which it forms a dark red solution. (Proust.)

C. Arseniate of Cobalt-oxide, or Cobalt-arseniate.—*a. Terbasic.*—Occurs in the form of *Cobalt-bloom*, which, according to Kersten, is produced only by the weathering of cobaltine, not of cobalt-glance. Long, needle-shaped, rhombic prisms. Sp. gr. 2·84 to 3·0; less hard than gypsum; varies from translucent to transparent; carmine, columbine, or peachblossom-coloured; yields a powder having the same colour. When exposed to the light, it sustains a slight loss of weight, probably from evolution of water, and becomes paler and opaque on the surface. When heated in a glass tube, it parts with its water, but does not give off arsenious acid; the last portions of water, however, are only driven off by continued strong ignition. The residue is of a smalt-blue colour, if free from iron, but an admixture of ferrous arseniate renders it green or brown. Green cobalt-bloom is anhydrous arseniate of cobalt-oxide containing iron. (Kersten, *Pogg.* 60, 251.) Cobalt-bloom, heated

on charcoal before the blowpipe, emits fumes of arsenic, and fuses in the inner flame into a green bead of arsenide of cobalt; it colours borax blue. When treated with hot potash-solution, cobalt-bloom yields a deposit of black protoxide, and a blue liquid, from which, on dilution with water, the dissolved cobalt is again separated. (Proust, Kersten.) Cobalt-bloom is insoluble in water, but dissolves with facility in hydrochloric or nitric acid, forming a red solution; its solution in nitric acid is not attended with separation of arsenious acid, or with evolution of nitric oxide on the application of heat. (Proust.) In ammonia it forms a deep red solution. It dissolves in a weak solution of green vitriol; and on evaporating the liquid, white crystalline ferrous arseniate separates out, while cobalt-sulphate remains in solution. (Kersten.) The salt may be obtained artificially, by precipitating a cobalt-salt with arseniate of soda: it then forms a peachblossom-coloured precipitate, which dries up to a dark, horny mass.

	Cobalt-bloom.				Kersten.		
	At.						*a.*
CoO	3	....	112·5	....	37·57	....	36·52
FeO		....		....		....	1·01
NiO		....		....		....	trace
AsO^5	1	....	115·0	....	38·39	....	38·43
HO	8	....	72·0	....	24·04	....	24·10
			299·5	....	100·00	....	100·06

							Kersten.
	At.						*b.*
CoO	8	....	300	....	33·48	....	33·42
FeO	1	....	35	....	3·91	....	4·01
NiO		....		....		....	
AsO^5	3	....	345	....	38·50	....	38·30
HO	24	....	216	....	24·11	....	24·09
			896	....	100·00	....	99·82

							Kersten.
	At.						*c.*
CaO	3	....	84·0	....	7·18	....	8·00
CoO	9	....	337·5	....	28·86	....	29·19
AsO^5	4	....	460·0	....	39·33	....	38·10
HO	32	....	288·0	....	24·63	....	23·90
			1169·5	....	100·00	....	99·19

a. is from the Wolfgang-Maassen mine, near Schneeberg;—*b.* from the Rappold mine, near Schneeberg;—*c.* from the Daniel mine, near Schneeberg. This peculiar variety *c*, in which part of the cobalt is replaced by lime, occurs in small, pearly, light rose-coloured, spherical masses, made up of needle-shaped, diverging crystals; it yields a white powder. When heated, it becomes violet but does not evolve arsenious acid. *a*, *b*, and *c* were dried at 100° before analysis. The formula: $3CoO,AsO^5+8Aq$. corresponds to that of Vivianite (p. 224). Kersten.

Cobalt-coating, Kobaltbeschlag.—Botryoidal; kidney-shaped or massive; scaly or earthy; opaque, and varying in colour from peachblossom-red to pale rose-colour. Produced by the weathering of cobaltine, on which it immediately rests. May be regarded as a mixture of cobalt-bloom and arsenious acid, often with a small quantity of cobalt-sulphate superadded. When gently heated, it first gives off water, then a large quantity of arsenious acid, but no metallic arsenic, and a violet (dirty

brown, if iron is present) residue, which dissolves in nitric acid, but (unless iron is present) without evolution of nitric oxide. The solution contains arsenic acid, cobalt-oxide, and ferric oxide, but no arsenious acid. Hot water extracts the arsenious acid from this mineral, together with any cobalt-sulphate that may be present. The residue formed when the arsenious acid is extracted from cobalt-coating by the water of the mines, consists of cobalt-bloom. (Kersten, *Pogg.* 60, 251.)

Kersten.

	a.	*b.*	*c.*	*d.*
CoO	16·60	18·30		
FeO	2·10			
AsO^5	19·10	20·00		
HO	11·90	12·13	12·4	12·5
AsO^3	51·00	48·10	53·2	50·1
CaO		trace		
NiO	trace	trace		
SO^3	trace	trace		
	99·70	98·53		

a. is Cobalt-coating, from the Wolfgang-Maassen mine at Schneeberg;—*b.* from the Röhling mine at Annaberg;—*c.* and *d.* from the Daniel mine at Schneeberg.

A basic arseniate of cobalt-oxide is found in commerce: 1. Prepared in the humid way; *Chaux métallique.* Carbonate of potash is added to a solution of cobalt-glance in nitric acid or aqua-regia, as long as a white precipitate of ferric arseniate continues to form, and the filtrate further treated with carbonate of potash, to precipitate the arseniate of cobalt-oxide.—2. Cobalt-glance is fused with twice its weight of potash; the fused mass exhausted with water, which takes up sulphide of potassium, together with arsenic, iron, and potassium; the white regulus again fused with potash; the resulting blue slag used for the preparation of smalt (p. 346); and the arsenide of cobalt, which is thus obtained free from iron, is pulverized, and then roasted, first at a gentle heat, and afterwards at an intense heat, till it is converted into a reddish powder.

b. Acid Salt.—The solution of the hydrate or terbasic arseniate of cobalt-oxide in excess of arsenic acid, yields, by evaporation in vacuo, peachblossom-coloured needles, arranged in stellate masses, and united in spherules, resembling cobalt-bloom but soluble in water. If pieces of calcspar are suspended in the solution by a wire, small carmine-coloured needles, principally consisting of arseniate of lime, attach themselves to the calcspar. (Kersten, *Pogg.* 60, 266.)

D. Sulpharsenite of Cobalt.—$2CoS,AsS^3$.—Dark brown precipitate, which gradually but completely settles down from the liquid, becomes black when dry, and dissolves in excess of the sodium compound. By distillation it yields orpiment, and leaves a grey, metallic, unfused mass, still containing sulphur and arsenic, and probably analogous to cobalt-glance. (Berzelius.)

E. Sulpharseniate of Cobalt.—$2CoS, AsS^5$.—Dark brown precipitate, black after drying, soluble in excess of the sodium-compound used as a precipitant, and forming a dark brown solution. (Berzelius.)

F. Sulphide of Cobalt with Arsenide of Cobalt.—*Cobalt-glance.*—Belongs to the regular system, *Figs.* 1, 2, 5, 18, 19. Cleavage

parallel to the cube-faces. Harder than apatite. Sp. gr. 6·2 to 6·3. Reddish silver-white, yielding a greyish-black powder.—Not altered by heating out of contact of air; when strongly ignited in an open tube, it gives off arsenious and sulphurous acid, and, according to Scheerer, leaves a dingy violet powder. When heated on charcoal before the blowpipe it emits a strong arsenical fume, and, after roasting for some time, may be fused to a greyish-white, brittle mass of arsenide of cobalt. After roasting it colours borax blue. (Berzelius.) Cobalt-glance heated to whiteness in a charcoal crucible, is first converted, with a loss of 32·2 per cent. of AsS^2 (realgar), into Co^2As, 2CoS:

$$2(CoAs,CoS^2) = AsS^2 + Co^4AsS^2;$$

afterwards, by the continued application of a very intense heat, sulphur is evolved [in the form of bisulphide of carbon ?], and a residue of Co^4As left behind, which, however, generally retains 5 or 6 per cent. of sulphur. 100 parts of cobalt-glance ignited at a moderate heat with 500 parts of lead yield: *a.* 398 parts of lead (containing 97 per cent. of lead together with sulphur, arsenic, cobalt, iron, and copper); and *b.* 64·5 of arsenide of cobalt (containing 41·46 p. c. cobalt, 34·38 arsenic, 1·24 sulphur, and small quantities of iron, copper, and quartz). (Berthier, *Ann. Chim. Phys.* 62, 116; also *J. pr. Chem.* 10, 15.) Cobalt-glance dissolves in nitric acid with evolution of heat and separation of arsenious acid.

	At.	*Cobalt-glance.*		Stromeyer. Skütternd.
Co	2	59	35·54	33·10
Fe				
As	1	75	45·18	43·47
S	2	32	19·28	20·08
		166	100·00	96·65

	Hubert.		Patera.	Ebbinghaus.	Schnabel.		
	a.	*b.*	*c.*	*d.*	*e.*	*f.*
Co	30·37	32·02	32·07	33·71	29·77	8·67
Fe	5·75	4·56	3·42	1·62	6·38	25·98
Sb						2·84
As	44·13	43·63	42·97	45·31	44·75	42·53
S	19·75	19·79	20·25	19·35	19·10	19·98
Quartz			1·63			
	100·00	100·00	100·34	99·99	100·00	100·00

¶ *a.* Massive cobalt-glance from Orawitcza in Upper Hungary.—*b.* A fibrous variety from the same locality. These two varieties contain veins of gold and native bismuth; the bismuth amounting to 18 per cent. may be removed by the saw.—*c.* Cobalt-glance from Skütternd.—*d.* From the *Morgenröthe* mine at Siegen, previously regarded as massive *Scheidkobalt.* —*e.* Cobalt-glance in microscopic but distinct crystals, from the *Philippshoffnung* mine at Siegen.—*f.* An ore from the *Green Lion* mine at Siegen, formerly denominated *Fibrous Earthy Cobalt.* (*Jahresber, L. & K.* 1847-8, 1155; 1849, 720.)

Many kinds of arsenical pyrites also contain cobalt. A variety from Huaseo in Chili, previously denominated *Glaucodote* by Breithaupt, has been found by Plattner to contain, in 100 parts,

S.	As.	Co.	Ni.	Fe.	SiO^2.
20·210	43·200	24·774	trace	11·900	trace.

C. Sulphate of Cobalt-oxide and Zinc-oxide.—Large, red, four-sided prisms, which disintegrate in the air and yield a white powder. (Link, *Crell. Ann.* 1790, 1, 32.)

Cobalt and Tin.

A. Alloy.—Light violet-coloured, somewhat ductile.

B. Stannate of Cobalt-oxide.—By mixing stannate of potash with a dissolved cobalt-salt. Bluish precipitate, which becomes reddish by washing; dark brown and conchoidal in the fracture by drying; flesh-coloured by pulverization; black by ignition; and light blue by exposure to a white heat. (Berzelius.)

Cobalt and Iron.

Alloy.—Very hard and difficult to break.

Other Compounds of Cobalt.

With Nickel, Copper, Mercury, and Gold.

Chapter XXXIV.

NICKEL.

Cronstedt, *Abhandl. der Schwed. Akad. der Wissensch.* 1751, 293, and 1794, 38.
Bergman, de Niccolo, *Opusc.* 2, 231; 3, 459; 4, 374.
Richter, *A. Gehl.* 2, 61; 3, 244 and 444; 51, 699.
Bucholz, *A. Gehl.* 2, 282; 3, 201,
Thénard, *Ann. Chim.* 50, 117; also *A. Gehl.* 4, 281.
Proust, *J. Phys.* 57, 169; 63, 442; also *A. Gehl.* 2, 53; *N. Gehl.* 3, 435.
Tupputi, *Ann. Chim.* 78, 133; 79, 153.
Lampadius, *Schw.* 10, 114.
Laugier, *Ann. Chim. Phys.* 9, 267; also *N. Tr.* 3, 2, 93.
Berthier, *Ann. Chim. Phys.* 13, 52; also *Schw.* 28, 148.—*Ann. Chim. Phys.* 33, 49; also *Schw.* 48, 262.—*Ann. Chim. Phys.* 25, 94; also *Schw.* 42, 89.
Berzelius, *Schw.* 32, 156.
Lassaigne, *Ann. Chim. Phys.* 21, 255; also *N. Tr.* 9, 1, 180; abstr. *Schw.* 39, 108.
Erdmann, *Ueber das Nickel und Weisskupfer*, Leipzig, 1827. *J. pr. Chem.* 7, 248.

—precipitates all the iron, cobalt, and nickel with carbonate of soda—washes the precipitate thoroughly, and treats it first with oxalic acid and then with ammonia, as described on page 319, repeating the solution of the nickel-oxalate in aqueous ammonia, till the liquid which stands above the resulting precipitate no longer exhibits a rose-colour, and is almost wholly free from cobalt.

2. Berthier dissolves roasted cobalt-speiss or roasted copper-nickel—together with the quantity of iron found by previous experiments to be necessary for the separation of the arsenic acid—in boiling aqua-regia containing excess of nitric acid; evaporates the solution to dryness; treats the residue with water, which leaves a large quantity of ferric arseniate undissolved; and adds carbonate of soda to the filtrate, stirring all the while, till the precipitate begins to exhibit a green tint: the whole of the ferric arseniate is thereby thrown down, together with part of the cupric oxide. If the precipitate, which is white at first, does not ultimately turn brown, it is a sign that the quantity of ferric oxide present is not sufficient to carry down the arsenic acid with it; consequently, more sesquichloride of iron must be added, and the ferric oxide again cautiously precipitated by carbonate of soda. The filtrate is next treated with sulphuretted hydrogen to precipitate the rest of the copper; the liquid, filtered from the sulphide of copper, completely precipitated at a boiling heat by carbonate of soda; the precipitate, consisting of the carbonates of nickel and cobalt, thoroughly washed and diffused in water; chlorine gas passed through the liquid as long as it is absorbed; the solution exposed to the air to allow the excess of chlorine to evaporate, and then filtered. The filtrate contains chloride of nickel free from cobalt; it may be precipitated by an alkali. The whole of the cobalt remains on the filter in the form of protoxide, together with a portion of the nickel in the form of peroxide. If the cobalt were in excess, the residue on the filter would certainly consist wholly of cobalt-oxide; but in that case, chloride of cobalt would likewise be found in the filtrate.—Berthier's older method differs from the preceding in the following particulars: No iron is added to the ore of nickel which is to be dissolved, but the solution obtained by evaporating to dryness and digesting the residue in water, is first mixed with carbonate of soda till the precipitate (of ferric arseniate) which is white at first, begins to show colour—then filtered—mixed with a quantity of ferric chloride sufficient to separate the arsenic acid—and again cautiously treated with carbonate of soda, which first throws down ferric arseniate together with oxide of copper, and afterwards hydrated ferric oxide. The liquid is then filtered, and the rest of the iron precipitated, together with the nickel and cobalt, in order that the precipitate may be treated by Laugier's method, with oxalic acid and ammonia; or the iron and cobalt are first thrown down by the cautious addition of carbonate of soda—then a mixture of cobalt and nickel—then, after filtration, pure nickel. If manganese is present, the last precipitation must be made in the cold, otherwise the manganese will not be retained in solution.

Tupputi dissolves the pounded speiss in $2\frac{1}{2}$ parts of nitric acid and an equal quantity of water, whereupon the sulphur separates out; evaporates the solution till the greater part of the arsenious acid is precipitated; filters; and mixes it while yet warm with carbonate of soda or potash, stirring all the while, till the precipitate—which is at first yellowish-white, consisting of ferric arseniate, and afterwards rose-coloured, consisting of cobalt-arseniate, together with small quantities of cupric and manganous *arseniates*—begins to turn green. The solution is then filtered, mixed

with a small quantity of acid and a very large quantity of water, and the arsenic precipitated by sulphuretted hydrogen, the passage of the gas being continued till the liquid saturated with it retains its odour after being kept in a stoppered vessel for 24 hours; it is then again filtered, boiled, and the nickel precipitated in the form of carbonate by means of a carbonated alkali. According to Laugier, the nickel-arseniate goes down together with the cobalt-arseniate, and the nickel precipitate obtained at the end of the process is still mixed with cobalt and iron. The solution of the speiss in nitric acid may likewise be diluted with water, precipitated by sulphuretted hydrogen, and boiled—the filtrate [after further boiling to bring the iron to a higher state of oxidation] mixed with a quantity of potash sufficient to precipitate a small portion of the nickel, together with the whole of the iron, so that the precipitate appears brown after boiling for some time, but has green flakes mixed with it;—then heated with such a quantity of potash that the liquid merely retains a pale green colour—and afterwards boiled for half-an-hour. Since cobalt-oxide has a stronger affinity for nitric acid than nickel-oxide, the former is wholly taken up by the liquid, and the nickel-oxide is completely or almost completely precipitated. (Anthon, *Repert.* 59, 44.) This method is uncertain; if too much potash is added, or if too much cobalt is present, the cobalt is not completely dissolved on boiling; besides it becomes more highly oxidized on exposure to the air, and then no longer exerts a precipitating action on the oxide of nickel which remains in solution. (Berzelius, *Jahresber.* 18, 152.)

4. The roasted speiss is mixed with a quantity of nitric acid not sufficient to dissolve it—the liquid diluted with water, after the action has gone on for a sufficient length of time, either in the cold or with the aid of heat—then decanted from the precipitated basic bismuth-salt, and heated to the boiling point (on the large scale, it is boiled in a copper vessel). Milk of lime is then added in small portions, till a filtered sample exhibits, no longer a pale green, but a bluish-green colour, and gives with potash a precipitate, which, when heated on charcoal before the blowpipe, yields an infusible mass of spongy nickel. As long as the reduced nickel continues fusible, arsenic is present, and further addition of lime is necessary; it is best to add the lime in slight excess, in order to insure the complete separation of the arsenic.—The liquid is then filtered, and the nickel precipitated by milk of lime free from iron. (Erdmann.)

5. Proust heats roasted copper-nickel with dilute sulphuric acid, and adds carbonate of potash to the filtered solution, to precipitate arseniate of ferric oxide, till iron can no longer be detected in the liquid by ferrocyanide of potassium. The liquid is then filtered again, and sulphuretted hydrogen passed through it, to precipitate arsenic, copper, and bismuth, till it is so far saturated as to retain the odour of the gas after being kept for 24 hours in a closed vessel. The liquid, once more filtered and then evaporated, yields crystals chiefly consisting of sulphate of nickel-oxide and potash, while the cobalt-salt, for the most part, remains in solution; the former is repeatedly dissolved and recrystallized to free it from adhering cobalt-salt, and its solution afterwards treated with carbonate of potash, which precipitates the nickel in the form of carbonate.—Thomson (*Ann. Phil.* 14, 144) digests pounded speiss with dilute sulphuric acid, frequently adding nitric acid as long as the latter exhibits any action; he then decants the green solution from the arsenious acid, then evaporates and cools it, whereupon nearly pure nickel-sulphate separates

out. The mother-liquid, no longer capable of yielding crystals, is freed from arsenious acid by sulphuretted hydrogen, and when subsequently evaporated, again deposits crystals of nickel-sulphate. The whole of the crystals are then purified by repeated solution and crystallization, and the salt afterwards decomposed by carbonate of potash.

6. The roasted speiss is made up into a paste with oil of vitriol, and exposed to a heat, gentle at first, but gradually rising to redness, in order to decompose the remaining sulphates. The mass, while still hot, is then exhausted with water; sulphate of potash (the residue of the nitric acid manufacture) is dissolved in the heated filtrate; the liquid evaporated and cooled till it yields crystals of nickel-oxide and potash; the crystals gently ignited to render the adhering ferric arseniate insoluble, and afterwards dissolved in water; and carbonate of nickel-oxide precipitated from the filtrate by the addition of carbonate of potash. This process yields perfectly pure nickel, but the sulphuric acid does not extract the whole of the nickel from the speiss; moreover, the crystallization is tedious.

7. One part of carefully roasted speiss is mixed with 1 pt. of pounded fluorspar, and from 3 to 3½ pts. of oil of vitriol, and heated in a leaden vessel to a temperature above 100°, the mixture being constantly stirred, and the heat continued till it is dry; care must be taken not to inhale any vapour of fluoride of arsenic. It is then taken out, broken up, and burnt at a moderate heat in a reverberatory furnace; the product exhausted with boiling water; the liquid filtered from the gypsum; and the ferric oxide contained in it precipitated in the ordinary way. The filtrate still gives a yellow precipitate with sulphuretted hydrogen, but the precipitate does not contain arsenic. (Liebig, *Pogg.* 18, 166.) Further purification from lime and cobalt is required. According to Duflos, a platinum dish must be used instead of the leaden vessel, if it be required to drive off all the arsenic, because the lead reduces part of the arsenic to the metallic state.

8. Roasted speiss is dissolved in strong hydrochloric acid, the liquid filtered and evaporated to dryness, and the residue heated nearly to redness, and afterwards exhausted with water. Arseniate of ferric oxide is then left undissolved, accompanied by the arseniates of nickel- and cobalt-oxide, if the quantity of ferric oxide added is not sufficient to take up the whole of the arsenic acid. The solution contains chloride of nickel, which, however, requires further purification. (Berzelius.)

9. Roasted speiss is digested in hydrochloric acid, which leaves nothing undissolved but 3 or 4 per cent. of sulphur, and a few granules which have retained the metallic state; the liquid is diluted with water, and separated by filtration from the precipitated oxychloride of bismuth; the filtrate heated to the boiling point; aqueous sesquichloride of iron added to it, and then milk of lime in small portions—the boiling being still continued, till a sample taken out of it exhibits the characters described in (4); and the nickel precipitated from the filtrate by milk of lime free from iron. In applying this method also, it is better to use too much chloride of iron and milk of lime, than too little; it is preferable to the 4th and 6th methods, and may be used in the preparation on the large scale. (Erdmann.)

10. Unroasted cobalt-speiss is treated as described in the preparation of cobalt (p. 318, 6); the resulting sulphide of nickel (which appears free from arsenic after being once fused with sulphur and carbonate of potash,

and then washed out with water) dissolved in nitric or nitrosulphuric acid, and subjected to further treatment. (Wöhler, *Pogg.* 6, 227.)

11. One hundred parts of pounded speiss are fused with 40 parts of nitre. The mixture becomes red-hot, swells up a little, and fuses completely at a stronger heat, yielding (1) an upper layer of slag, which is brown, translucent, crystalline, and consists of sulphate of potash, with a small quantity of cobalt; (2) a compact, greyish-black, lower stratum of slag, containing small quantities of cobalt and iron: and (3) a regulus amounting to 84 parts, and consisting chiefly of nickel and arsenic. —This, when pulverized and again ignited with 33·6 parts of nitre, yields (1) a partly blue, partly greyish-black slag, containing iron, cobalt, and a small quantity of nickel; and (2) a regulus amounting to 58·8 parts, partly divided into granules.—This, when again fused with 23·5 parts of nitre, yields a greyish-green slag, rich in nickel, but poor in cobalt, and a regulus amounting to 35·3 parts, and consisting wholly of nickel and arsenic. In the third fusion, a somewhat smaller quantity of nitre may be used, in order to avoid the loss of nickel.—To obtain pure nickel from the arsenide thus produced, three methods may be adopted: (*a.*) The pounded regulus is roasted as long as arsenic continues to be evolved; the residue, together with $\frac{1}{10}$th of iron, is dissolved in aqua-regia; the solution evaporated to dryness at a gentle heat; the residue dissolved in water, which leaves the greater part of the ferric arseniate undissolved; the remainder of the ferric arseniate precipitated from the filtrate by cautious addition of carbonate of ammonia; the liquid filtered from this precipitate, treated with sulphuretted hydrogen to precipitate any copper or lead that may be present; the solution again filtered and evaporated to dryness; and pure protoxide of nickel obtained from the residue by ignition.—(*b.*) 1 part of pounded arsenide of nickel is fused with $1\frac{1}{2}$ pts. nitre and 2 pts. carbonate of potash (or with 8 or 10 parts of litharge, or with a much smaller quantity of lead-nitrate); the fused mass washed with water; the residue, together with a small quantity of iron, dissolved in nitric acid; the solution treated as in *a*; and finally the nickel precipitated by carbonate of soda.—(*c.*) 1 pt. of arsenide of nickel is fused at a white heat with $1\frac{1}{2}$ pt. dry carbonate of soda, 1 pt. sulphur, and $\frac{1}{10}$ charcoal; the sulphide of nickel, which unites into a cake, separated from the slag, and again fused in the same manner with $\frac{1}{2}$ pt. carbonate of soda, 1 sulphur, and $\frac{1}{10}$ charcoal; the cake separated from the slag, repeatedly exhausted with water, which still takes up a large quantity of sulpharseniate of sodium, and leaves the nickel-sulphide in the form of metallic spangles; and finally acted upon by dilute sulphuric acid, which does not attack the sulphide of nickel. The sulphide of nickel thus purified, is dissolved in aqua-regia; the liquid evaporated to dryness; the residue digested in water; any copper and lead that may be present, precipitated by sulphuretted hydrogen; the liquid filtered and evaporated; and pure nickel-oxide obtained from the residue by ignition. (Berthier.)

12. One part of unroasted speiss in the state of fine powder is mixed with 2 pts. litharge, and rapidly heated in the wind-furnace till it fuses. The sulphur burns; the more oxidable metals are converted into slag; and the less oxidable nickel settles at the bottom, in combination with arsenic. If it still contains cobalt, the latter is removed by pounding the regulus very finely, sifting it through fine silk, and again fusing it with 1 or 2 pts. of litharge. 100 parts of speiss thus treated yield from 50 to 60 parts of pure arsenide of nickel, which may be treated as in (10). The cobalt and nickel contained in the lead-slag produced in this process may likewise be separated out. (Berthier, *Ann. Chim. Phys.* 33, 49.)

13. Hermbstadt's method (p. 319) may likewise be applied to the separation of nickel.

14. Commercial oxide of nickel may be purified by digesting it in a quantity of hydrochloric acid not quite sufficient to dissolve it (the ferruginous nickel-oxide is then left undissolved); treating the filtrate with sulphuretted hydrogen, to precipitate copper and arsenic; filtering again and boiling, with addition of nitric acid at last, to bring the iron to a higher state of oxidation; mixing the solution with acetate of potash, and boiling again to precipitate the ferric oxide completely; and passing sulphuretted hydrogen through the filtrate, whereby the greater part of the nickel is precipitated, together with a trace of cobalt. The remaining portions of the nickel and cobalt may be obtained from the filtrate by precipitating with sulphide of ammonium which has turned yellow; digesting in acetic acid, which re-dissolves the manganese; and collecting the precipitate on a filter. (Wackenroder, *N. Br. Arch.* 16, 128.)

¶ 15. The following method is adopted in a manufactory at Birmingham for separating nickel and cobalt from the Hungarian speiss, containing 6 per cent. of nickel and 3 p. c. of cobalt. The ore is first fused with chalk and fluorspar—the slag thrown away—and the fused product ground to powder, and roasted for 12 hours in a reverberatory furnace, till no more fumes of arsenious acid are given off. The roasted product then dissolves almost completely in hydrochloric acid. The solution is diluted with water, mixed with chloride of lime, to convert the iron into sesquioxide, and with milk of lime to precipitate that oxide together with the arsenic. The precipitate (which is of no further use) is then washed, and sulphuretted hydrogen passed through the clear liquid, till a filtered sample gives a black precipitate on the addition of ammonia. The precipitated sulphides (which are likewise of no further use) having been washed with water, the solution is next treated with chloride of lime to precipitate the cobalt, and then with milk of lime to throw down the nickel. The cobalt-precipitate is converted either into sesquioxide by gentle ignition, or into protoxide by strong ignition, and sent into the market in one or other of these forms: it is said to be very pure. The precipitated nickel is reduced by charcoal, and sold to the manufacturers of German silver. (Louyet, *N. J. Pharm.* 15, 204.) ¶

For the *separation of Nickel from Cobalt,* the methods described on pages 319, 320, may be used. With regard to method (4) the following is to be observed: The acid solution mixed with cyanide of potassium till the precipitate re-dissolves, and then gently warmed, is to be boiled for at least an hour with a very large excess of hydrochloric acid; by this means the precipitated cyanide of nickel is dissolved in the form of chloride, while double cyanide of cobalt and nickel remains upon the filter. (Liebig.) To separate *Nickel from Manganese,* the acid solution is mixed with a sufficient quantity of acetate of soda; the greater part of the nickel precipitated by sulphuretted hydrogen; the filtrate freed by evaporation from the greater part of the excess of acid, then largely diluted, and the metals precipitated by sulphide of ammonium added in large excess. The mixture is then supersaturated with acetic acid, which re-dissolves the precipitated sulphide of manganese, and the sulphide of nickel collected after a few minutes on the filter, and washed with water containing sulphuretted hydrogen. (Wackenroder, *N. Br. Arch.* 16, 126.) The second method for the separation of cobalt from manganese may likewise be applied in this case.

Reduction.—1. Pure protoxide of nickel, or its carbonate, is introduced into a covered charcoal crucible—either alone or made up into a stiff paste with oil, and, according to Berthier and Erdmann, under a layer of glass—and exposed to the heat of a blast-furnace. The nickel thus reduced takes up a small quantity of carbon, and likewise forms more or less nickel-graphite. If the fire be kept as low as possible, the reduction gradually extends from without inwards, and a grey, porous nickel is formed, containing but little carbon. When large quantities are to be reduced, a mixture of 100 parts nickel-oxide and 8 or 10 charcoal powder is closely pressed into an unluted earthen crucible, and very strongly ignited. (Berthier.)—2. The same mixture is heated alone in the pottery-furnace. (Richter.) In this case, carbonic oxide is the reducing agent. —3. Or it is exposed to the flame of the oxyhydrogen blowpipe. —4. Hydrogen gas is passed over the ignited oxide. In this case the metal remains pulverulent.—5. Oxalate of nickel-oxide, or oxalate of nickel-oxide and ammonia, is heated to redness under a stratum of pounded glass not containing any heavy metal. (Döbereiner, Berzelius.)

Properties.—Fused nickel reduced by (1) has a density of 8·38 (Tupputi), the density of that obtained by (2) is 8·279 according to Richter, and 8·402 according to Tourte (*N. Gehl.* 7, 442); of that prepared by (5), the density is 8·637 (Brunner, *Kastn. Arch.* 14, 177); while that reduced by (1) has a density of 9·0, according to Vauquelin and Hauy. Hammered nickel reduced by (1) has a density of 8·82 (Tupputi), and the density of that obtained by (2) is 8·666 according to Richter, and 8·932 according to Tourte.—Nickel reduced by (2) is hard and susceptible of a high polish, perfectly ductile, and may be hammered, either cold or hot, into plates $\frac{1}{100}$ of an inch in thickness, and drawn out into wires $\frac{1}{80}$ of an inch in diameter. (Richter.) It wears a file very rapidly. When bent, it becomes hot and exhibits an indented fracture (Tourte.) Its malleability is diminished by admixture of carbon or manganese. Nickel obtained by (1) is often less ductile than zinc (Tupputi); it is brittle in the cold, somewhat extensible at a red heat: that obtained by (5) yields to the hammer at first, but afterwards flies asunder, into pieces exhibiting a strongly lustrous, coarse-grained fracture (Brunner); it is brittle. (Geitner, *Schw.* 48, 147.)—The colour of nickel is silver-white, inclining to steel-grey; it has a strong lustre. According to Richter, nickel may be welded; but according to Tourte, it welds but imperfectly. Nickel obtained by (2) is at least as difficult of fusion as manganese. (*Richter.*) That obtained by (1) [probably from admixture of carbon] fuses more readily than manganese (Tupputi); as easily as cast-iron (Erdmann). That obtained by (1) contracts strongly in solidifying, so that the solid mass exhibits a depression on its upper surface. (Gm.)—It is attracted by the magnet, and may be rendered magnetic by the same means as iron. According to Tupputi, its magnetic power is somewhat less than that of iron; according to Lampadius, the magnetic power of nickel is to that of iron as 35 : 55; according to Wollaston, as 2—3 : 8—9. Its magnetic power is destroyed by repeated ignition. (Tourte.)

Compounds of Nickel.

NICKEL AND OXYGEN.

A. NICKEL-OXIDE. NiO.

Protoxide of Nickel, Nickeloxydul; formerly *Nickeloxyd.*

Formation.—1. Nickel does not oxidate in the air at ordinary temperatures, even though the air be damp (Richter); at a higher temperature, it tarnishes on the surface, and exhibits different colours, like steel (Tourte), and at a red heat becomes covered with a greenish-grey oxide. When kept at a red heat for a considerable time, it is almost wholly converted into a brown, brittle mass, which is either a mixture of the protoxide with metallic nickel—inasmuch as it is attracted by the magnet—or a suboxide. (Tupputi.) Nickel reduced by hydrogen at a gentle heat takes fire when exposed to the air after cooling. (Magnus.) On a glowing coal fed with oxygen gas, nickel burns with emission of vivid sparks (Tourte); and a nickel wire introduced into oxygen gas with a piece of red-hot charcoal at the end, burns for a short time with emission of sparks. (Berzelius.)—2. Nickel does not decompose water at ordinary temperatures. (Tupputi.) At a red heat, it decomposes aqueous vapour very slowly, becoming covered with finely crystallized oxide of a light olive-green colour. (Regnault, *Ann. Chim. Phys.* 62, 352.) It dissolves very slowly, and with evolution of hydrogen, in dilute phosphoric, sulphuric, or hydrochloric acid, hydrogen being evolved and a salt of the protoxide formed. (Tupputi.)—3. Nitric acid oxidizes nickel very easily, with evolution of nitric oxide gas; heated oil of vitriol (according to Tupputi) oxidizes it with great difficulty, sulphurous acid being evolved. The oxide of nickel formed in these cases unites with the acid.—4. Red-hot nickel is oxidized by nitre.

Preparation.—By igniting the hydrated oxide or the carbonate in a close vessel. The protoxide of nickel thus obtained is mixed with peroxide, from which it may be freed by heating it to 100° in a stream of hydrogen. (Erdmann.)

Properties.—Small crystals of a light olive-green colour (Regnault, *vid. sup.*); green-greyish yellow powder (Erdmann); when formed at a white heat, it is an olive-green powder (Berthier). Blackish-grey. (Tupputi.) Not magnetic. Specific gravity of the crystallized oxide, 6·605. (Genth.)

					Klaproth.		Richter.		Thomson.
Ni	29·5	....	78·67	....	77	....	77·82	....	78
O	8·0	....	21·33	....	23	....	22·18	....	22
NiO	37·5	....	100·00	....	100	....	100·00	....	100

	Rothoff.		Tupputi.		Proust.		Lassaigne.
Ni	78·555	....	78·7	....	80	....	83·33
O	21·445	....	21·3	....	20	....	16·66
	100·000	....	100·0	....	100	....	100·00

Decompositions.—Reduced to the metallic state by ignition with charcoal, carbonic oxide gas, or hydrogen gas, or with potassium or sodium (at

of nickel (or of cobalt) sets hydrogen free, and precipitates the whole of the metal in the form of a black magnetic powder. (Becquerel.) Zinc added to a solution of nickel throws down green flakes and liberates hydrogen till a double salt of zinc and nickel is formed. (Tupputi.) Fischer (*Pogg.* 9, 265; 22, 495) likewise obtained green gummy flakes with cadmium and tin, but not when the nitrate of nickel-oxide was used.

Hydrosulphuric acid produces no precipitate in solutions of nickel-oxide in the stronger mineral acids, unless the acid is saturated as completely as possible; in that case, it throws down a small quantity of black hydrated sulphide of nickel; but the slightest excess of acid prevents the precipitation. From nickel-salts containing vegetable acids—the acetate, for example—hydrosulphuric acid throws down the greater part of the nickel. Acetate of nickel-oxide is completely precipitated by hydrosulphuric acid. (Robiquet, *Ann. Chim. Phys.* 69, 285.) According to Wackenroder, the precipitation is not quite complete, and ceases as soon as the excess of acetic acid reaches a certain limit. Nickel-salts containing mineral acids, but converted into acetates by the addition of acetate of soda, are almost entirely decomposed by hydrosulphuric acid. The sulphide of nickel, when once precipitated, is but very sparingly re-dissolved by dilute mineral acids—somewhat more freely by cold concentrated acids—and scarcely, if at all, by dilute acetic acid. Hence strongly acidulated nickel solutions yield a permanent precipitate with an alkaline hydrosulphate even in very small quantity. (Wackenroder, *N. Br. Arch.* 16, 123.) Alkaline hydrosulphates precipitate nickel-salts completely; hydrosulphate of ammonia, however, retains a portion of the sulphide of nickel in solution—for a while at least—forming a dark-coloured liquid. The hydrosulphate of ammonia, in proportion as it is converted by contact with the air into hydrosulphite, deposits sulphide of nickel, probably containing more than one atom of sulphur, and therefore insoluble in hydrosulphate of ammonia. Hence chloride of nickel supersaturated with ammonia, forms, with hydrosulphate of ammonia, a liquid which is black [brown] at first, but slowly becomes clear by exposure to the air (immediately on the addition of acetic acid). Hydrosulphate of ammonia containing hydrosulphite (*e. g. Beguin's* Spirit) precipitates nickel-solutions, either acid or ammoniacal, completely and immediately, so that a colourless filtrate is obtained. (Wackenroder.) Hydrated sulphide of manganese and sulphide of cobalt likewise throw down hydrated sulphide of nickel from solutions of nickel-salts. (Anthon.)

Ammonia added in small quantity, even to neutral nickel-salts, produces but a very slight turbidity, and when its quantity is increased, changes the green colour of the solution more and more to blue, and ultimately to violet. The violet liquid may be supposed to contain ammoniacal oxide of nickel (niccolate of ammonia) together with another nickel-salt. So long as the quantity of ammonia is less than sufficient to saturate both the acid contained in the nickel-salt and the oxide of nickel, the liquid probably contains a certain quantity of undecomposed nickel-salt, as well as niccolate of ammonia and the other ammoniacal salt. The blue liquid, when exposed to the air, deposits, in proportion as it gives off ammonia and takes up carbonic acid, a green compound of carbonic acid, nickel-oxide, and ammonia.—Potash and soda added to nickel-salts completely precipitate the oxide in the form of an apple-green hydrate, containing a portion of the alkali, but insoluble in excess. —Carbonate of ammonia, potash, or soda, throws down a pale green precipitate, which is but slightly soluble in excess of carbonate of soda, even

when very highly concentrated, but easily soluble in carbonate of ammonia, with which it forms a greenish-blue solution.—Chlorine passed through the liquid converts the precipitate into hydrated peroxide, but does not dissolve it.—The carbonates of baryta, strontia, lime, and magnesia, do not precipitate nickel-salts in the cold, but completely on boiling. (Demarçay.) According to Fuchs (*Schw.* 62, 191), carbonate of lime produces no precipitate in nickel-salts, even at a boiling heat.—Hydrated cobalt-oxide boiled with nickel-salts throws down hydrated oxide of nickel. (Anthon.)—Hydrated lead-oxide likewise decomposes the hydrochlorate and nitrate of lead-oxide at a boiling heat, and hydrated stannous oxide and mercuric oxide decompose the hydrochlorate. (Demarçay, *Ann. Pharm.* 11, 251.)—Phosphate of soda forms a greenish-white precipitate with nickel-salts.—Sulphite of potash (but not sulphite of ammonia) at a boiling heat precipitates part of the oxide in the form of a basic salt. (Berthier.)

Oxalic acid (not oxalate of potash) gradually decomposes the salts of nickel, throwing down nearly all the oxide in the form of a greenish-white, pulverulemt oxalate.—Hydrocyanic acid added to solutions of nickel in the weaker acids, completely precipitates the nickel in the form of white pulverulent cyanide. It decomposes the acetate completely—the salts containing mineral acids partially—and the sulphate of nickel-oxide and potash not at all by itself, but completely on the addition of acetate of soda; in the latter case, however, an excess of hydrocyanic acid re-dissolves the precipitate. Cyanide of potassium precipitates all salts of nickel, but an excess of it renders the solution clear again.—Tincture of galls gives no precipitate with the sulphate or chloride of nickel, but with the acetate it forms a thick brownish-yellow precipitate.

Those nickel-salts, which are insoluble in water, dissolve for the most part in hydrochloric or sulphuric acid.—The salts of nickel form double salts with many salts of ammonia, potash, and soda.

c. With ammonia, the fixed alkalis, the earths, and many heavy metallic oxides, as lead-oxide, ferrous oxide, ferric oxide, &c.,—inasmuch as the aqueous fixed alkalis added to an ammoniacal solution of nickel (niccolate of ammonia) throw down a compound of nickel-oxide and potash (niccolate of potash);—and when an acid solution of nickel-oxide and magnesia, alumina, lead-oxide, ferrous oxide, or ferric oxide is supersaturated with ammonia, the latter is unable to take up all the nickel.

B. Peroxide of Nickel. Ni^2O^3.

Nickelschwärze, or *Black earthy Nickel*, is perhaps an impure form of this compound.

Preparation.—1. By heating the nitrate of nickel-oxide not quite to redness. (Berzelius.)—2. By gently heating the carbonate in an open vessel. (Proust.)

Black powder, the specific gravity of which, according to Herapath, is 4·846.

					Rothoff.		Lassaigne.
2Ni	59	....	71·08	....	70·95	....	71·43
3O	24	....	28·92	....	29·05	....	28·57
Ni^2O^3	83	....	100·00	....	100·00	....	100·00

At a red heat, this compound gives off oxygen, and is converted into the protoxide; it dissolves in nitric and sulphuric acid, with evolution of

oxygen—in hydrochloric acid, with separation of chlorine—and in aqueous ammonia, with evolution of bubbles of nitrogen gas: in all these cases, a solution of the protoxide is formed. (Proust, Winkelblech, *Ann. Pharm.* 13. 259.)

Hydrated Peroxide of Nickel.—1. Formed by passing chlorine gas through water in which the hydrate or carbonate of nickel-oxide is suspended; with the anhydrous oxide the action is slower. (Proust, Lassaigue.) A third of the nickel dissolves in the form of chloride:

$$3NiO + Cl = Ni^2O^3 + NiCl.$$

2. By heating one of the three compounds just mentioned with aqueous chloride of lime (Proust, Böttger) or chloride of soda (Demarçay). Bromine-water likewise converts the protoxide of nickel into bromide and peroxide (Balard); and when a nickel-salt is placed in the circuit of a voltaic battery consisting of at least 100 pairs of plates, peroxide of nickel [hydrated ?] collects on the positive pole. (Fischer, *Kastn. Arch.* 16, 219.)

Black mass, having a shining, conchoidal fracture; when diffused in water, it appears dark brown.

					Winkelblech.
2Ni	59	....	53·64	....	53·84
3O	24	....	21·82	....	22·03
3HO	27	....	24·54	....	24·13
Ni^2O^3,3HO	110	....	100·00	....	100·00

The hydrate, when heated to redness, gives off oxygen and water, and leaves protoxide of nickel. All acids dissolve it with violence, and convert it into a salt of the protoxide; with cold aqueous oxalic acid, it is quickly converted into carbonic acid gas and green pulverulent nickel-oxalate. (Winkelblech.)—It may be boiled with caustic potash or soda without undergoing decomposition; but when boiled with water containing a trace of acid, it gives off oxygen with violent effervescence. (Demarçay, *Ann. Pharm.* 11, 251.)

Nickel and Carbon.

A. Carbide of Nickel.—*a.* To this head belongs the nickel described at (1) page 361, obtained by reducing the protoxide with charcoal.—*b.* Nickel fused upon charcoal before the oxy-hydrogen blowpipe, takes up carbon, which renders it brittle, and gives it a brass-yellow colour; but it remains magnetic. (Döbereiner, *N. Tr.* 4, 1, 293.)—*c.* The magnetic residue obtained on igniting the cyanide of nickel, is either a mixture or a compound of nickel and carbon.—*d. Nickel-graphite.*—When nickel is reduced with charcoal, the resulting metallic button is found to be covered with softly crystalline, steel-grey scales, which leave a stain when rubbed, are greasy to the touch, and dissolve in nitric acid. (Will. Ross, & Irving, *Ann. Phil.* 18, 62, and 149.) Probably pure carbon.

B. Carbonate of Nickel-oxide, or Nickel-Carbonate.—¶. *a. Basic Carbonate.*—*a. Emerald-nickel, Nickelsmaragd.*—Occurs in the form of a stalactitic crust on chrome-iron-ore in Texas, and in Lancaster county, Pennsylvania; known to American mineralogists, since 1846, by the name of *Green-oxide of Chromium.* Amorphous, with an uneven, somewhat scaly

fracture. Hardness between calcspar and fluorspar. Sp. gr. from 2·57 to 2·693. Emerald-green, with strong vitreous lustre and yellowish-green streak. Heated in a flask, it gives off water, and turns blackish-grey. Dissolves readily in hydrochloric acid, leaving a residue of chrome-iron. (*Sill. Am. J.* [2], 6, 248.)

	Emerald-nickel.		Sillman.
3NiO	112·5	59·73	58·82
Co^2	22·0	11·66	11·69
6HO	54·0	28·61	29·49
$NiO,CO^2+2(NiO,3HO)$	188·5	100·00	100·00

β. *Hydro-nickel-magnesite.*—A mineral allied to the preceding, and occurring in the same localities, on serpentine. It contains magnesia in addition to the preceding constituents. It has not been analyzed quantitatively. (Shepard, *Sill. Am. J.* [2] 6, 250.) ¶

b. Monocarbonate.—The protoxide and its hydrate absorb carbonic acid from the air, and acquire a green colour in consequence. (Proust.)

When a nickel-salt is precipitated by an alkaline carbonate, pale apple-green flakes are obtained, which, after washing and drying, sometimes form a loose, earthy, pale green mass, having a faint metallic taste, sometimes, especially after continued washing with boiling water, a thick blackish-green mass, having a conchoidal, waxy fracture.—The salt thus obtained is always basic; but its proportions of base, acid, and water vary considerably, accordingly as monocarbonate or bicarbonate of potash has been used as the precipitant, and according to the composition and temperature of the mixture, and the temperature of the wash-water; this will be seen from the following statements: *a.* Precipitated by bicarbonate of potash: greenish-white, falls to pieces, and forms a white powder when exposed to sunshine.—*b.* Precipitated by monocarbonate of potash. (Berthier.) [These precipitates were probably merely dried in the air.]—*c.* Precipitated by bicarbonate of potash from a tolerably concentrated solution of chloride of nickel kept in constant ebullition. The gelatinous precipitate, after being washed with warm water, shrinks together strongly on drying; it is green and dotted with white specks; dried over oil of vitriol in vacuo.—*d.* The dilute solution precipitated with a slight excess of monocarbonate of potash. One part α washed with cold, the other β with boiling water; both dried in vacuo over oil of vitriol.—*e.* Precipitated from a tolerably concentrated and boiling solution with twice the quantity of monocarbonate of potash required for precipitation; the precipitate after drying in the air, loses no more weight by drying in vacuo.—*f.* The same as *d*, but the solution more dilute, and the precipitate washed with boiling water; dried as above.—*g.* Precipitated from a moderately-concentrated solution by carbonate of potash; the precipitate merely dried in the air. (Setterberg, *Pogg.* 19, 56.)

	a.	*b.*	*c.*	*d,α.*	*d,β.*	*e.*	*f.*	*g.*
NiO	48·3	47·5	67·47	69·50	71·60	73·69	81·58	68·78
CO^2	21·0	14·0	14·89	5·15	5·23	11·06	2·99	3·17
HO	30·7	38·5	17·64	25·35	23·17	15·25	15·43	28·05
	100·0	100·0	100·00	100·00	100·00	100·00	100·00	100·00

Nickel and Boron.

Borate of Nickel-oxide.—Borax throws down from nickel salts a pale apple-green powder, not soluble in water, but soluble in sulphuric, hydrochloric, and nitric acid (Tupputi); it fuses into a hyacinth-coloured glass. (Berzelius.)—Sexborate of soda likewise forms a greenish precipitate with nickel-salts.

Nickel and Phosphorus.

A. Phosphide of Nickel.—*a. Containing but a small quantity of Phosphorus.*—1. Formed by passing phosphorus vapour over red-hot nickel (H. Davy); or by throwing pieces of phosphorus on red-hot nickel (Pelletier).—2. By fusing nickel with glacial phosphoric acid and charcoal powder (Pelletier); or from 6 to 8 parts of nickel-filings or nickel-oxide in a charcoal crucible with 10 pts. bone-ash, 5 quartz-powder, and 1 charcoal (Berthier).—Silver-white, brittle; exhibits an acicular structure, according to Pelletier—laminar, according to Lampadius and Berthier. Much more fusible than nickel; not magnetic. The phosphorus burns when the compound is heated in the air.

	Pelletier.	Lampadius.
Ni	83	87
P	17	13
	100	100

b. Triphosphide.—1. By heating chloride of nickel in a current of phosphuretted hydrogen gas.—2. Similarly, with sulphide of nickel.—Prepared by (1); black, insoluble in hydrochloric acid, but easily decomposed by and dissolved in nitric acid. (H. Rose, *Pogg.* 24, 322.)

			H. Rose.
3Ni	88·5	73·81	72·41
P	31·4	26·19	27·59
Ni^3P	116·9	100·00	100·00

B. Hypophosphite of Nickel-oxide, or Nickel-hypophosphite.—The solution prepared like that of the corresponding cobalt-salt, and evaporated in vacuo, yields less distinct green crystals, which appear to be cubes. These crystals, when heated in a retort, give off water at first and turn yellow—then swell up violently, and give off a gas which does not take fire spontaneously, but blackens silver-solution strongly, and burns with a bright phosphorus-flame when set on fire—and finally leave a residue of nickel-phosphate blackened by the admixture of some phosphoric compound, and insoluble in hydrochloric acid. (H. Rose, *Pogg.* 12, 91.)

C. Phosphite of Nickel-oxide, or Nickel-phosphite.—Terchloride of phosphorus dissolved in water, neutralized by ammonia, and then mixed with a neutral solution of chloride of nickel, deposits this salt, after a while, in crystalline scales. The mother-liquid, which is still somewhat greenish, and likewise the greenish wash-water, yield an additional precipitate when boiled, but still retain a slight greenish tint. The dried

salt heated in a retort, is decomposed without visible combustion, and yields water and hydrogen gas free from phosphorus. (H. Rose, *Pogg.* 9, 41.)

D. PHOSPHATE OF NICKEL-OXIDE, or NICKEL-PHOSPHATE.—*a. Triphosphate ?*—By precipitating a nickel-salt with diphosphate of soda.—Pale apple-green flakes, or emerald-green crystalline granules.—By ignition in hydrogen gas, it is resolved into water and phosphide of nickel. Insoluble in water, but soluble in sulphuric hydrochloric, or nitric acid.

b. Acid Phosphate.—Concentrated phosphoric acid exerts no action on the metal, but the dilute acid, when heated, dissolves it with evolution of hydrogen.

E. PYROPHOSPHATE OF NICKEL-OXIDE.—Analogous to the cobalt-salt.

¶ Formed by decomposing sulphate of nickel-oxide with pyrophosphate of soda. Light green powder, yellow after ignition. Dissolves in mineral acids, in pyrophosphate of soda, and in ammonia. If the nickel contains cobalt, only the cobalt-compound is precipitated from the ammoniacal solution by alcohol, the nickel-salt remaining in solution. —On dissolving this salt in sulphurous acid and boiling, it is reprecipitated in the crystalline state; if it contains cobalt, a crystalline cobalt-salt is first thrown down, and afterwards the nickel-salt. The salt dried at 100° gives off 26·05 per cent. of water on ignition.

					Schwarzenberg.
2NiO	75·0	....	51·23	....	51·3
PO^5	71·4	....	48·77	....	48·7
$2NiO,bPO^5$	146·4	....	100·00	....	100·0

	Crystallized.				Schwarzenberg.
2NiO	75·0	....	37·42		
PO^5	71·4	....	35·63		
6HO	54·0	....	26·95	....	26·05
$2NiO,bPO^5 + 6Aq.$	200·4	....	100·00		

(Schwarzenberg, *Ann. Pharm.* 65, 158.)

F. METAPHOSPHATE OF NICKEL-OXIDE.—Formed by mixing sulphate of nickel-oxide with excess of dilute phosphoric acid, evaporating, and heating in a platinum capsule to 316°; it is then obtained in the form of a greenish-yellow powder, insoluble in water and dilute acids, but soluble in strong sulphuric acid.

					Maddrell.
NiO	37·5	....	34·48	....	34·40
PO^5	71·4	....	65·52	....	65·60
NiO,aPO^5	108·9	....	100·00	....	100·00

(Maddrell, *Ann. Pharm.* 61, 58.) ¶

NICKEL AND SULPHUR.

A. DISULPHIDE OF NICKEL.—Formed by passing hydrogen gas over sulphate of nickel-oxide at a red heat. Decomposition takes place quickly

with evolution of sulphurous acid and water, and finally, also of sulphuretted hydrogen. 100 parts of anhydrous nickel-sulphate leave 42·28 of disulphide of nickel.—Pale yellow, metallic, semifused, brittle; exhibits moderate magnetic power.—Dissolves in nitric acid, leaving a residue of sulphur; slowly in strong hydrochloric acid, with evolution of sulphuretted hydrogen [and pure hydrogen], but not in dilute hydrochloric acid, even when heated. (Arfvedson, *Pogg.* 1, 65.)—To this head probably belongs also the yellow-greyish-white, strongly lustrous, very brittle, and highly magnetic sulphide of nickel, which Berthier obtained by heating the sulphate to whiteness in a charcoal crucible; its fracture was laminar in one direction, but granular in all others; 100 parts of nickel-sulphate yielded only 52 pts. of the sulphide.

B. Protosulphide of Nickel.—Found native in the form of *Capillary Pyrites.—Preparation.*—1. Nickel and sulphur heated together combine, producing vivid incandescence. (Proust, H. Rose.) Combination takes place below the melting point of sulphur. Nickel-dust takes fire when thrown into a glass tube an inch wide, filled with sulphur vapour. A mixture of nickel-dust and milk of sulphur in equivalent proportions contained in a glass tube, takes fire when touched at the upper end with a glowing coal, and burns down to the bottom of the tube. (Winkelblech, *Ann. Pharm.* 20, 36.)—2. By heating nickel-oxide with sulphur. (Tupputi.)—3. By passing sulphuretted hydrogen over red-hot nickel-oxide, whereupon 100 parts of the oxide yields 121·3 parts of sulphide. (Arfvedson.)—4. By igniting hydrated sulphide of nickel out of contact of air. (Tupputi.)

By (1) and (2): Fused, bronze-yellow, brittle; exhibits an uneven fracture; not magnetic. (Tupputi, H. Rose.) By (3): Dark brown, non-magnetic powder, less fusible than the disulphide. (Arfvedson.)—By ignition in the air, it is converted into a green mass (basic sulphate of nickel-oxide?). When heated to redness in phosphuretted hydrogen gas, it is slowly decomposed, yielding phosphide of nickel and sulphuretted hydrogen (H. Rose); not decomposed by hydrogen gas at a red heat. (H. Rose, *Pogg.* 4, 129; Arfvedson.)—Gives off but a very small quantity of sulphur when ignited in a current of aqueous vapour. (Regnault, *Ann. Chim. Phys.* 62, 380.) Not decomposed by chlorine gas in the cold, and very slowly even when heated. (H. Rose, *Pogg.* 42, 540.)—Dissolves in nitric acid and aqua-regia, the sulphur being partly separated, and partly converted into sulphuric acid. Not soluble in hydrochloric or sulphuric acid.

Capillary pyrites occurs in capillary, regular six-sided prisms derived from an acute rhombohedron, whose faces often terminate the prisms. *Fig.* 151 and 154. Cleavage parallel to the faces of an acute rhombohedron; $r^3 : r^5 = 35° 52'$. Sp. gr. 5·278. (Miller, *Phil. Mag. J.* 6, 104; 20, 378.) Double six-sided pyramid, of specific gravity 5·00. (Breithaupt.) Sp. gr. 5·65. (Rammelsberg.) Harder than calcspar; brass-yellow, inclining to bronze-yellow. Heated on charcoal before the blowpipe, it gives off sulphurous acid, and fuses into a coagulated, ductile, magnetic mass of nickel (Berzelius); into a black bead (Kobell). After roasting, it behaves with fluxes like oxide of nickel. Dissolves with difficulty in nitric acid, easily in aqua-regia.

sulphide of nickel, and green, permanent crystals are obtained, having the form of hyposulphite of magnesia. They are converted, even below 100°, into a semifluid mass, which, as the temperature rises, gives off water, sulphurous acid, and sulphur, and leaves 32·73 per cent. of nickel-sulphide in the form of a yellow, agglomerated mass. (Rammelsberg, *Pogg.* 56, 306.)

	Crystallized.				Rammelsberg.
NiO	37·5	....	26·88	....	26·5
S^2O^2	48·0	....	34·41	....	
6HO	54·0	....	38·71	....	
$NiO, S^2O^2 + 6Aq.$	139·5	....	100·0		

E. Sulphite of Nickel-oxide, or Nickel-sulphite.—*a. Basic.*—Precipitated on boiling a nickel-salt with sulphite of potash; becomes more basic during washing. (Berthier.)—According to Böttinger (*Ann. Pharm.* 51, 406), the precipitates obtained by boiling nickel-salts with sulphite of ammonia always contain ammonia.

b. Monosulphite.—The crystals which separate from a solution of nickel in aqueous sulphurous acid (*vid. sup*). When strongly ignited, they leave a residue of 30·48 per cent. In the state of aqueous solution, they take up 101·85 parts of iodine. (Fordos & Gélis.)

Crystallized:	*Calculation,*		according to Fordos & Gélis.
NiO	37·5	....	30·36
SO^2	32·0	....	25·91
6HO	54·0	....	43·73
$NiO, SO^2 + 6Aq.$	123·5	....	100·00

¶ When sulphurous acid gas is passed through water in which a large quantity of hydrated nickel-oxide is suspended, the whole dissolves, and the solution yields a small quantity of a crystalline powder, which is no longer soluble in water, but dissolves in hydrochloric acid, with evolution of sulphurous acid. It contains 4 atoms of water.

					Muspratt.
NiO	37·5	....	35·55	....	35·52
SO^2	32·0	....	30·33	....	30·15
4HO	36·0	....	34·12	....	34·33
$NiO, SO^2 + 4Aq.$	105·5	....	100·00	....	100·00

The liquid filtered from this salt, when placed for some days in vacuo over sulphuric acid, yielded very fine tetrahedral crystals of the preceding salt, with 6 atoms of water. (Muspratt, *Ann. Pharm.* 50, 281.) ¶

F. Hyposulphate of Nickel-oxide, or Nickel-hyposulphate.—By decomposing hyposulphate of baryta with sulphate of nickel-oxide, and evaporating the filtrate, long green prisms are obtained, which are resolved by heat into sulphurous acid gas and sulphate of nickel-oxide. (Rammelsberg, *Pogg.* 56, 295.)

					Rammelsberg.
NiO	37·5	....	22·93	.....	22·02
S^2O^5	72·0	....	44·04		
6HO	54·0	....	33·03		
$NiO, S^2O^5 + 6Aq.$	163·5	....	100·00		

	R. Phillips.				Mitscherlich.			Thomson.
	rhomb.	*sq. prism.*	*rhomb.*		*sq. p. a.*		*b.*	*rhomb.*
NiO	26·30	26·2	54·4		30·14		29·88	24·64
SO^3	28·16	30·0						29·28
7HO	45·54	43·8	45·6					45·99
NiO,SO^3+7Aq.	100·00	100·0	100·0					99·63

The square prismatic salt *a.* examined by Mitscherlich, was obtained by crystallization from a warm solution; *b.*, by exposing the rhombic salt to the sun.

When hydrochloric acid gas is passed over (anhydrous?) nickel-sulphate, 2 atoms of the salt absorb 1 atom of hydrochloric acid, the absorption being attended with rise of temperature. The absorbed acid is immediately given off on the application of heat, and gradually on exposure to the air; and the aqueous solution yields crystals of pure nickel-sulphate, the hydrochloric acid remaining in the mother-liquid. (Kane, *Ann. Pharm.* 19, 5.)

H. Sulphocarbonate of Nickel.—Nickel-salts form, with aqueous sulphocarbonate of calcium, a dark brown-red mixture, which, in the course of 24 hours, deposits black flakes and becomes brownish-yellow. (Berzelius.)

Nickel and Selenium.

A. Selenite of Nickel-oxide, or Nickel-selenite.—*a. Monoselenite.*—By double decomposition. Insoluble in water, white when moist, but becomes apple-green when dry. (Berzelius.) ¶ According to Muspratt, on the contrary, it falls as a greenish-powder, on adding selenite of potash to sulphate of nickel-oxide, and becomes white when dried.

				Muspratt.
NiO	37·5		36·59	
SeO^2	56·0		54·63	
HO	9·0		8·78	9·17
NiO,SeO^2+Aq.	102·5		100·00	

(*Chem. Soc. Qu. J.* 64.) ¶

b. Biseleniate.—Green, gummy mass, soluble in water.

B. Seleniate of Nickel-oxide, or Nickel-seleniate.—Crystals isomorphous with those of nickel-sulphate, form 2, and with those of zinc-selenite. *Fig.* 37, $e : e'=138° 56'$; $e : e'=97° 4'$; $p : e=110° 32'$; $q : q=90°$; $e : q=131° 28$; p : *the face between* e and $e'=117° 54\frac{1}{2}'$; $p : e=126° 50'$, &c. (Mitscherlich, *Pogg.* 12, 124.)

Nickel and Iodine.

A. Iodide of Nickel.—1. Pulverulent nickel reduced by hydrogen, is heated with iodine in a glass tube, or vapour of iodine is passed over it. When the resulting iron-black, laminated mixture of nickel-iodide, metallic nickel, and nickel-oxide (the last produced by excess of air), is strongly ignited, pure iodide of nickel sublimes. Nickel in the coherent

state has no sensible action on iodine, even with the aid of heat.—2. The solution of nickel-oxide in aqueous hydriodic acid, leaves on evaporation a black, metal-shining residue, which, when ignited out of contact of air, sublimes without fusion or decomposition.

The sublimed iodide of nickel obtained by (1) and (2), presents the appearance of strongly lustrous, iron-black laminæ, resembling mica, and unctuous to the touch.—If the air has access to it during sublimation, a small quantity of grey-green oxide, free from iodine, is left behind. (Erdmann.) Lassaigne, by heating nickel with iodine, obtained a brown, fusible mass which dissolved in water, forming a green solution.

					Erdmann.		Lassaigne.
Ni	29·5	....	18·97	.....	18·56	....	23·81
I	126·0	....	81·03	.....	81·44	....	76·19
NiI	155·5	....	100·00	.....	100·00	....	100·00

Hydrated Iodide of Nickel, or Hydrate of Nickel-oxide.—Iodide of nickel soon becomes moist in the air, and forms a red-brown solution with a small quantity of water, and a green solution with a larger quantity. This solution evaporated to a syrup, yields bluish-green prisms, which quickly deliquesce in the air. The aqueous solution is capable of dissolving a large quantity of iodine (thereby becoming brown), and the iodine is given off again on boiling. (Erdmann, *J. pr. Chem.* 7, 254.)

	Crystallized.				Erdmann (*approximate.*)
NiI	155·5	.....	74·22	.....	72·82
6HO	54·0	.....	25·78	.....	27·18
NiI + 6Aq.	209·5	.....	100·00	.....	100·00

The crystals examined by Erdmann had still some mother-liquid adhering to them.

B. Hydrated Oxy-iodide of Nickel, or Terbasic Hydriodate of Nickel-oxide?—1. When a considerable quantity of aqueous nickel-oxide is evaporated to dryness, and the residue treated with water, a small quantity of this compound remains undissolved in the form of a red-brown powder. It often happens, however, that part of this residue is redissolved, together with the iodide of nickel, so that the solution appears brownish-green instead of pure green, smells of iodine, gives a blue colour with starch, and evolves iodine when evaporated.—2. Hydrate of nickel-oxide digested with aqueous iodide of nickel, takes up the iodide of nickel, and assumes a brown-red colour.—3. Similarly with carbonate of nickel-oxide, which thereupon gives off carbonic acid.—4. The compound is likewise formed by triturating hydrated nickel-oxide with an alcoholic solution of iodine.—When it is prepared by 2, 3, or 4, a certain quantity of hydrate or carbonate of nickel-oxide remains mixed with it, even if an excess of aqueous iodide of nickel or tincture of iodine has been used.—The red-brown powder is decomposed at a red heat, yielding vapour of iodine, vapour of water, and pure oxide of nickel. It dissolves in nitric acid, with evolution of iodine. Boiling potash extracts the whole of the iodine, leaving a dingy green residue of hydrated oxide. When immersed in aqueous ammonia, it assumes a dingy green colour without dissolving to any perceptible extent; but the ammonia takes up iodine, and assumes a blue colour. Boiling alcohol converts it into green hydrated oxide.

In acetic acid it forms a yellowish-green solution; with boiling aqueous oxalic acid, it yields oxalate of nickel-oxide. (Erdmann.)

					Erdmann (2.)
NiI	155·5	....	24·76	....	23·17 to 24·9
9NiO	337·5	....	53·74	....	52·80 ,, 54·7
15HO	135·0	....	21·50	....	24·00 ,, 20·4
NiI,9NiO + 15Aq.	628·0	....	100·00	....	99·97 ,, 100·0

C. Iodate of Nickel-oxide, or Nickel-iodate.—Iodate of potash gives no precipitate with nickel-salts. (Pleischl.)—The salt is formed by dissolving recently precipitated nickel-hydrate in aqueous hydriodic acid, and afterwards evaporating and cooling.—Light green crystalline powder, which gives off its water at 100°, and at higher temperatures evolves iodine vapour and oxygen gas, and leaves pure oxide of nickel. It dissolves in 120·3 parts of water at 15°, and in 77·35 pts. of boiling water. (Rammelsberg, *Pogg.* 44, 562.)

	Crystalline powder.				Rammelsberg.
NiO	37·5	....	17·65	.....	17·88
IO^5	166·0	....	78·12	.....	78·01
HO	9·0	....	4·23	.....	4·11
NiO,IO^5 + Aq.	212·5	....	100·00	.....	100·00

Nickel and Bromine.

A. Bromide of Nickel.—Nickel-filings heated to dull redness absorb bromine vapour, and turn brownish; at a stronger heat, the compound assumes an appearance like that of mosaic gold, and at a very bright red heat, it partly sublimes in yellow micaceous scales.—Bromide of nickel heated to bright redness in the air, is resolved into bromine vapour and oxide of nickel. Heated nitric acid decomposes it, and on evaporating the solution and igniting the residue, oxide of nickel is left behind. (Berthemot, *Ann. Chim. Phys.* 44, 389; also *J. Pharm.* 16, 655.)

					Berthemot.
Ni	29·5	....	27·34	.....	27·09
Br	78·4	....	72·66	.....	72·91
NiBr	107·9	....	100·00	.....	100·00

Hydrated Bromide of Nickel, or *Hydrobromate of Nickel-oxide.*—1. Bromide of nickel deliquesces in the air and dissolves in water; more slowly, however, after sublimation.—2. The hydrated bromide may also be formed by digesting nickel with bromine and water. (Berthemot.)—The resulting green solution turns brownish on evaporation, and yields small, dirty-white, very deliquescent needles. (Berthemot.) The crystals have the same green colour as other salts of nickel—give off water and turn yellow when placed within a receiver over oil of vitriol, and at 200°, gradually give off 20·15 per cent. of water. (Rammelsberg, *Pogg.* 55, 243.)—The aqueous solution, when exposed to the air, gradually deposits a few flakes of nickel-oxide; on evaporation, it leaves reddish bromide of nickel. (Berthemot.)

	Crystallized.		Rammelsberg.
NiBr	107·9	79·98	79·85
3HO	27·0	20·02	20·15
NiBr + 3Aq.	134·9	100·00	100·00

Bromide of nickel dissolves in hydrochloric acid, ammonia, alcohol, and ether. (Berthemot.)

B. Bromide of Nickel-oxide, or Nickel-bromate.—Formed by precipitating sulphate of nickel-oxide with bromate of baryta, and evaporating the filtrate under a bell-jar beside oil of vitriol.—Beautiful regular octohedrons.—The crystals when heated, first give off water, then decompose with violence, evolving bromine and oxygen gas, and leave 16·47 per cent. of nickel-oxide. They dissolve in 3·58 parts of cold water. (Rammelsberg, *Pogg.* 55, 69.)

Anhydrous.			*Crystallized.*			Rammelsberg.
NiO	37·5	24·05	NiO	37·5	17·86	16·47
BrO^5	118·4	75·95	BrO^5	118·4	56·41	
			6HO	54·0	25·73	
NiO, BrO^5	155·9	100·00	+ 6Aq.	209·9	100·00	

Nickel and Chlorine.

A. Chloride of Nickel.—1. Finely divided nickel heated to low redness in a stream of chlorine, burns with a vivid glow, and forms yellow, crystalline scales resembling mosaic gold. (H. Rose, *Pogg.* 20, 156.) Chloride of nickel, sublimed for the most part, is likewise formed, together with chloride of sulphur, on decomposing sulphide of nickel with chlorine gas. (Fellenberg.)—2. By evaporating the aqueous solution of chloride of nickel or hydrochlorate of nickel-oxide, to complete dryness. (Proust.) The chloride of nickel thus obtained by evaporation, may be converted into the sublimed chloride by ignition in a retort. A small quantity of chlorine is evolved during this operation, being set free by the oxygen of the air. The spangles of the chloride fly about in the retort as they rise. If the heat be continued for some time, the whole of the chloride sublimes; but if it be applied for a shorter time only, part of the chloride remains at the bottom, in a mass resembling mosaic gold, containing numerous small crystals, and grey nodules of nickel-oxide on the sides. (Erdmann.)

Sublimed chloride of nickel presents the appearance of soft crystalline scales, which feel like mica, are of a pale yellow when separate, but appear golden-yellow in the mass. (Proust, Bucholz, Erdmann, Fellenberg.) The chloride obtained by evaporation is a brownish-yellow, earthy mass. (Proust, Erdmann.)—Chloride of nickel may be repeatedly sublimed without fusing. In vacuo, the sublimation takes places altogether without decomposition; but when the compound is sublimed in vessels containing air, a small quantity of chlorine is set free, and small grey nodules of nickel-oxide are formed on the sides of the vessel. (Erdmann.) Hence, by continued gentle ignition in the air, chloride of nickel is converted into a greyish-green powder of nickel-oxide free from chlorine. (Erdmann.) Chloride of nickel is very easily reduced to the metallic state by hydrogen gas at high temperatures; by phosphuretted

hydrogen it is decomposed as easily as chloride of copper, yielding phosphide of nickel and hydrochloric acid gas; by fusion with phosphorus, it yields phosphide of nickel and chloride of phosphorus. (H. Rose, *Pogg.* 27, 117.) Sublimed chloride of nickel is converted into the hydrated oxide by boiling with caustic potash; but it requires long boiling to render the conversion complete. Ammonia, even when the air is completely excluded, dissolves it slowly but completely, forming a blue solution. (Erdmann.) A few observations not perfectly correct, made by Bucholz, induced him to believe that sublimed chloride of nickel contains less chlorine than that obtained by evaporation. Lassaigne, on the other hand, concludes from his own analysis, that the sublimed chloride contains more than 1 At. chlorine to 1 At. nickel. Both these views are disproved by the above-mentioned observations of Erdmann, and by the following analyses made by that chemist:

			Erdmann.				Berthier.		Lassaigne.	
			Sublimed.	*By evaporation.*					*Sub.*	*By evap.*
Ni	29·5	45·45	45·25	45·33	45·3				33·33	52·63
Cl	35·4	54·55	54·75	54·67	54·7				66·67	47·37
NiCl	64·9	100·00	100·00	100·00	100·0				100·00	100·00

Hydrated Chloride of Nickel, or *Hydrochlorate of Nickel-oxide.*—1. Chloride of nickel obtained by evaporation quickly attracts water from the air, acquiring first a lemon-yellow, and then a green colour; it dissolves in water with considerable rise of temperature. If the evaporation has been carried too far, flakes of nickel-oxide remain dissolved. (Erdmann.) Sublimed chloride of nickel becomes light green by two days' exposure to the air, and afterwards dissolves readily in water. (Proust, H. Rose.) But if it has not been exposed to the air, it dissolves very slowly (Fellenberg), and only when boiled for a long time in the water: even hot hydrochloric acid dissolves it with difficulty. (Proust.)—2. The same liquid is produced by dissolving nickel in aqua-regia (hydrochloric acid dissolves it very slowly), or the oxide, hydrate, or carbonate in hydrochloric acid, to saturation. The solution, evaporated and cooled, yields granular, grass-green crystals—apparently short, four-sided prisms—which deliquesce or effloresce very slightly in the air, according to the quantity of moisture contained in it, and dissolve in 1½ pt. or 2 pts. of cold water, and likewise in alcohol. (Tupputi.) The solution is decomposed by hypochlorous acid, yielding chlorine gas and a precipitate of peroxide. (Balard.)

	Crystallized.		Proust.
NiCl	64·9	44·48	45
9HO	81·0	55·52	55
NiCl + 9Aq	145·9	100·00	100

B. Hydrated Oxychloride of Nickel, or Basic Hydrochlorate of Nickel-oxide.—Sparingly soluble in water; turns reddened litmus-paper blue. (Berzelius.)

¶ C. Chlorate of Nickel-oxide.—$NiO,ClO^5 + 6Aq$.—Crystallizes in beautiful regular octohedrons, of a deep green colour. Deliquescent, soluble in alcohol. Resolved by heat into chlorine, oxygen, and a residue of oxide with chloride of nickel: at a strong red heat, pure oxide of nickel remains behind. (Wächter, *Ann. Pharm.* 52, 233.) ¶

Nickel and Fluorine.

The *Fluoride* and *Oxyfluoride of Nickel* exhibit characters similar to those of the corresponding cobalt-salts, excepting that they are pale green instead of red. (Berzelius.)

Nickel and Nitrogen.

A. *Nitride of Nickel?*—A greasy nickel compound may be obtained by a process similar to that described for the preparation of nitride of zinc (p. 33).

B. Nitrate of Nickel-oxide, or Nickel-nitrate.—*a. Basic salt.*—Formed by heating the mononitrate to a certain point. Yellowish-green powder, insoluble in water. Contains 88 parts of nickel-oxide to 12 acid. (Proust.)

b. Mononitrate.—The metal dissolves quickly in nitric acid, with rise of temperature and evolution of nitrous gas. The dehydrated salt is yellow. When heated, it is first converted into the basic salt; then, according to Proust, into protoxide of nickel, or, according to Berzelius, into peroxide, if only gently heated. In combination with water, it forms emerald-green, octagonal prisms (Tupputi), or rhomboidal crystals (Bergman), which give off their water when heated, effloresce slightly or deliquesce rapidly in the air, according to the quantity of moisture contained in it, and are soluble in 2 parts of cold water, and likewise in alcohol. (Tupputi.)

Anhydrous.			*Crystallized.* *Calculation*, according to Millon.			Proust.
NiO	37·5	40·98	NiO	37·5	25·78	25
NO^5	54·0	59·02	NO^5	54·0	37·11	55
			6HO	54·0	37·11	20
NiO,NO^5	91·5	100·00	+6Aq.	145·5	100·00	100

C. Niccolate of Ammonia.—Aqueous ammonia dissolves the anhydrous oxide very slowly; the hydrated peroxide somewhat more quickly, with evolution of nitrogen gas; and the hydrated protoxide very quickly, leaving, however, a few green flakes. The liquid is violet-blue if the ammonia is in excess, lavender-blue if it contains a larger quantity of nickel, and azure-blue when completely saturated. On the application of heat, it is decomposed, with evolution of ammonia, and deposits hydrated nickel-oxide in crystalline grains. When exposed to the air, it deposits green flakes of carbonate of nickel-oxide and ammonia with excess of nickel-oxide, till the liquid thereby loses the whole of the nickel contained in it, and becomes completely decolorized. If, however, one of the stronger acids is present, the nickel remains dissolved in the form of a double salt. (Tupputi.) The fixed alkalis added to the solution throw down a compound of nickel-oxide with the fixed alkali.

D. Carbonate of Nickel-oxide and Ammonia.—*a. With excess of carbonate of ammonia.*—Carbonate of nickel-oxide dissolves in aqueous carbonate of ammonia, forming a greenish-blue solution.

b. With excess of Nickel-carbonate.—Deposited in the form of pale green, insoluble flakes, when aqueous niccolate of ammonia, or the liquid *a* just mentioned, is exposed to the air. (Tupputi.)

E. Phosphate of Nickel-oxide and Ammonia.—The ammoniacal solution of nickel-phosphate, boiled as long as ammonia is given off, deposits pale apple-green flakes, which contain nickel-oxide and ammonia, together with phosphoric acid. (Tupputi.) Alcohol added to the solution of nickel-phosphate in ammonia precipitates a light bluish-green powder, likewise containing ammonia; and if the alcohol be placed in a layer above the ammoniacal solution, the precipitate assumes the form of crystalline grains. (Erdmann.) The ammoniacal solution of metaphosphate of nickel-oxide exposed to the air, deposits all the nickel, first as a greyish, afterwards as a fine green precipitate. (Persoz, *Ann. Chim. Phys.* 56, 333.)

F. Hydrosulphate of Nickel-oxide and Ammonia.—Hydrated sulphide of nickel dissolves sparingly in ammonia and hydrosulphate of ammonia, forming a yellowish-brown solution.

G. Ammonio-hyposulphite of Nickel-oxide.—A concentrated solution of nickel-hyposulphite is supersaturated with ammonia; the blue liquid mixed with absolute alcohol; and the resulting blue crystalline powder washed with alcohol, pressed between paper, and quickly enclosed in well-stopped bottles. It soon turns green when exposed to the air. (Rammelsberg, *Pogg.* 56, 306.)

					Rammelsberg.
$2NH^3$	34·0	....	19·59	.....	21·98
NiO	37·5	....	21·62	.....	21·27
S^2O^2	48·0	....	27·67		
6HO	54·0	....	31·12		
$2NH^3 + NiO, S^2O^2 + 6Aq.$	173·5	....	100·00		

H. Ammonio-hyposulphate of Nickel-oxide.—On mixing the aqueous solution of nickel-hyposulphate with ammonia, this salt is precipitated in the form of a blue crystalline powder, which, by solution in warm ammonia and cooling, may be obtained in purer crystals. Small prisms of a fine violet-blue colour, reduced to laminæ by the predominance of two of the lateral faces. When heated in a tube, it first gives off ammonia, then sulphite and sulphate of ammonia, and leaves a partly yellow, partly black mixture of sulphide of nickel and sulphate of nickel-oxide. Decomposed by water, with evolution of ammonia and precipitation of nickel-oxide. (Rammelsberg, *Pogg.* 58, 295.)

					Rammelsberg.
$3NH^3$	51·0	....	31·78	.....	30·09
NiO	37·5	....	23·36	.....	23·36
S^2O^5	72·0	....	44·86		
$3NH^3 + NiO, S^2O^5$	160·5	....	100·00		

I. Ammonio-sulphate of Nickel-oxide.—Anhydrous nickel-sulphate absorbs 65·91 per cent. of ammonia, very rapidly, with great rise of temperature and considerable intumescence, and is thereby converted into a pale violet-white powder. Any water that may be present is driven out in the course of the absorption, probably in consequence of the rise of temperature. The powder, when moderately heated, gives off

a large quantity of ammonia, together with small quantities of water and sulphite of ammonia; and the yellow residue dissolves in water, with the exception of some reduced nickel, which remains in the form of a black powder. After sudden heating, the residue is blackened in some places by the presence of reduced nickel. The powder dissolves in water, forming a blue solution, with separation of green hydrated oxide of nickel. (H. Rose, *Pogg.* 20, 151.)

			H. Rose.
$3NH^3$	51·0	39·69	39·73
NiO,SO^3	77·5	60·31	60·27
$3NH^3+NiO,SO^3$	128·5	100·00	100·00

K. Niccolo-sulphate of Ammonia.—The dark blue solution of crystallized nickel-sulphate in the strongest aqueous ammonia, deposits crystals in the cold. It may also be evaporated to the crystallizing point in vacuo over oil of vitriol, or precipitated by alcohol, the light blue precipitate redissolved in the smallest possible quantity of warm water, and the salt left to crystallize by cooling. Transparent, dark blue, rectangular prisms, with dihedral summits resting on the narrow lateral faces. The crystals obtained by evaporation in vacuo have a more bluish-green colour, arising from enclosed mother-liquid. The crystals crumble to a light blue powder in the air or in vacuo. When heated in a glass tube, they yield ammonia, sulphate of ammonia, and a greyish-green powder, probably consisting of basic nickel-sulphate. They dissolve readily in water, forming a blue solution. The concentrated solution evolves ammonia when boiled, and deposits green flakes of hydrated oxide, which still retains sulphuric acid, even after long washing. Insoluble in alcohol, even when dilute. (Erdmann.)

	Crystallized.		Erdmann.
$2NH^3$	34·0	26·26	23·71
NiO	37·5	28·96	28·62
SO^3	40·0	30·88	30·83
$2HO$	18·0	13·90	16·84
$NH^4O,NiO+NH^4O,SO^3$	129·5	100·00	100·00

L. Sulphate of Nickel-oxide and Ammonia.—Formed by mixing sulphate of nickel-oxide with sulphate of ammonia. Bluish-green crystals, having the form of sulphate of magnesia and ammonia. (Mitscherlich.) Specific gravity 1·801, according to Thomson; 1·915 according to Kopp. Soluble in 4 parts of cold water. (Link, *Crell. Ann.* 1796, 1, 32.)

	Crystallized;—Mitscherlich's calculation.	
NH^3	17·0	8·61
NiO	37·5	18·99
$2SO^3$	80·0	40·51
$7HO$	63·0	31·89
$NH^4O,SO^3+NiO,SO^3+6Aq.$	197·5	100·00

M. Ammonio-iodide of Nickel.—*a. Terbasic.*—The saturated solution of nickel-iodide in water yields, when supersaturated with ammonia, whitish flakes, which dissolve slowly on the application of heat, forming first a reddish, and afterwards a light blue solution. (Erdmann.) The flakes are light blue, and dissolve when heated, leaving merely a small green residue. (Rammelsberg.) The blue solution when cooled (or mixed with alcohol: *Rammelsberg*) becomes completely decolorized, and deposits

the compound *a*, partly in the form of a light blue, heavy, crystalline powder, partly in small, blue, shining octohedrons. These crystals, when heated, give off ammonia and sal-ammoniac, then turn black, evolve iodine, and leave a compound of oxide and iodide of nickel. (Erdmann.) At 100°, they give off a small quantity of water; at a stronger heat, ammonia with more or less water; and the unfused residue, which is red-brown at first, and afterwards turns blackish-green, consists of pure iodide of nickel. (Rammelsberg.) The water is probably not essential, but cannot be completely expelled without decomposition of the compound. The salt gives off ammonia when exposed to the air, becoming first green and afterwards brown. It dissolves in water—with separation of light green flakes of hydrated oxide, containing very little iodine and no ammonia—and forms a blue liquid, which, after a while, again deposits crystals of the same compound. (Rammelsberg, *Pogg.* 48, 119.) It dissolves very sparingly in excess of ammonia. (Erdmann.)

	Crystallized.				Erdmann. *After deducting the water.*		
$3NH^3$	51·0	....	24·69	.....	22·67	.....	23·08
NiI	155·5	....	75·31	.....	75·57	.....	76·92
HO		....		.....	1·76		
$3NH^3$, NiI	206·5	....	100·00	.....	100·00	.....	100·00

b. Bibasic.—Iodide of nickel does not absorb ammoniacal gas in the cold; but when gently heated, it absorbs 18·151 per cent., becoming heated and swelling up to a yellowish-white mass. (Rammelsberg.)

					Rammelsberg.
$2NH^3$	34·0	....	17·94	.....	15·36
NiI	155·5	....	82·06	.....	84·64
$2NH^3$, NiI	189·5	....	100·00	.....	100·00

N. Niccolo-iodate of Ammonia.—Alcohol added to the blue solution of nickel-iodate in ammonia, throws down small crystals, or a light blue crystalline powder, which behaves very much like the corresponding cobalt-compound, and appears to consist of $2NH^3+NiO,IO^5$ [or $NH^3,NiO+NH^3,IO^5$]. (Rammelsberg, *Pogg.* 44, 562.)

O. Ammonio-bromide of Nickel.—1. Pulverized anhydrous bromide of nickel immersed in ammoniacal gas is converted into a pale violet powder. —2. A concentrated aqueous solution of bromide of nickel heated with excess of ammonia, yields a blue liquid, from which, as it cools, a light blue crystalline powder of the same composition is deposited. The compound obtained by (1) or (2) gives off its ammonia when heated; it dissolves in a small quantity of water, forming a blue solution; but on further addition of water, hydrated nickel-oxide is precipitated, and the liquid retains a pale blue colour. (Rammelsberg, *Pogg.* 55, 243.)

					Rammelsberg. (1)		(2)
$3NH^3$	51·0	....	32·10	.....	30·74	.....	30·95
Ni	29·5	....	18·56	.....	69·26	.....	19·37
Br	78·4	....	49·34				
$3NH^3$, NiBr	158·9	....	100·00	.....	100·00		

P. Ammonio-bromate of Nickel-oxide.—Formed by precipitating the concentrated solution of nickel-bromate in ammonia with alcohol.—Pale green crystalline powder.—When heated, it makes a hissing noise, giving off bromine vapour, oxygen gas, and nitrogen gas, and a sublimate of hydrobromate of ammonia, while a mixture of oxide and bromide of nickel is left behind. When boiled for some time with potash, it gives off the whole of its ammonia. When it is digested in water, the smaller part dissolves undecomposed and forms a blue solution, while the remaining portion is decomposed, with separation of green flakes of hydrated oxide. (Rammelsberg, *Pogg.* 55, 69.)

Q. Ammonio-chloride of Nickel.—1. Chloride of nickel, at ordinary temperatures, absorbs 74·84 per cent. of dry ammonia, with rise of temperature and tumefaction, and is converted into a white powder having a faint tinge of violet. The powder, when heated to redness, gives off ammoniacal gas, together with a small quantity of sal-ammoniac, and leaves chloride of nickel mixed with a little metallic nickel. It dissolves in water, forming a bluish solution, leaving, however, an undissolved residue of green hydrated oxide. (H. Rose, *Pogg.* 20, 155.)—2. The solution of chloride of nickel in aqueous ammonia yields, on the addition of alcohol, a light blue powder, and on cooling, large opaque octohedrons with truncated edges and summits, having a blue colour with violet iridescence. When heated in vacuo, they decrepitate and crumble to a yellow powder, giving off a trace of water, then ammonia, and leaving a residue of chloride of nickel. At a strong red heat, a sublimate of sal-ammoniac and chloride of nickel is obtained, and the residual chloride of nickel is mixed with a small quantity of metallic nickel; if the air has access, oxide of nickel remains behind. In warm air, or in vacuo over oil of vitriol, the crystals soon crumble to a yellow powder. They dissolve in cold water without decomposition; but the solution, when boiled, evolves ammonia and deposits green flakes of hydrated oxide free from chlorine. Insoluble in alcohol. (Erdmann, *J. pr. Chem.* 7, 266; 19, 445.)

					H. Rose. (1)		Erdmann. (2)
$3NH^3$	51·0	....	44·00	.....	42·81		
Ni	29·5	....	25·45	.....	57·19	....	25·2
Cl	35·4	....	30·55				30·3
$3NH^3,NiCl$	115·9	....	100·00	.....	100·00		

R. Chloride of Nickel and Ammonium.—Formed by mixing aqueous chloride of nickel with sal-ammoniac.—Green, imperfectly crystallized. (Tupputi.) ¶ By saturating 2 pts. of hydrochloric acid with nickel-oxide and 1 pt. of the same acid with ammonia—concentrating the mixed solution by slow evaporation, and leaving it to itself in a dry atmosphere for several days,—large, beautiful green crystals are obtained belonging to the oblique prismatic system.

					Hautz.
NH^4	18·0	....	6·17	.....	5·65
2Ni	59·0	....	20·30	.....	20·05
3Cl	106·2	....	36·44	.....	36·44
12HO	108·0	....	37·09	.....	37·86
$NH^4Cl,2NiCl+12Aq.$	291·2	....	100·00	.....	100·00

(Hautz, *Ann. Pharm.* 66, 283.) ¶

S. Fluoride of Nickel and Ammonium.—Granular crystals, easily soluble in water.

T. Niccolo-nitrate of Ammonia.—1. The concentrated solution of normal nickel-nitrate in ammonia, yields, at a freezing temperature, large, sapphire-blue, transparent, regular octohedrons, some of which have their summits truncated. The salt may likewise be precipitated from its solution by absolute alcohol; but as it is somewhat soluble in dilute alcohol, the salt thus obtained is smaller in quantity, and in the form of a granular precipitate, which requires to be washed with alcohol.—The crystals, when exposed to the air, give off ammonia, and gradually crumble to a bluish-white powder, which partially deliquesces in a damp atmosphere. They fuse when heated, first giving off water and ammonia, and afterwards nitrous vapours with slight detonation, and leave a residue of pure oxide of nickel. Heated in the air on platinum foil, they burn with tolerably strong detonation, leaving black protoxide of nickel, partly mixed with peroxide. They dissolve readily in cold water. The blue solution gives off ammonia on boiling, and deposits flakes of pure hydrated oxide, while nitrate of ammonia remains in solution. The dilute solution decomposes very quickly even as it begins to boil; the concentrated solution remains blue even when boiled. (Erdmann.)

	Crystallized.				Erdmann.
$2NH^3$	34·0	....	25·28	.....	27·16
NiO	37·5	....	27·88	.....	27·52
NO^5	54·0	....	40·14	.....	38·89
HO	9·0	....	6·70	.....	6·43
$NH^3, NiO + NH^4O, NO^5$	134·5	....	100·00	.....	100·00

U. Nitrate of Nickel-oxide and Ammonia.—Green, indistinct crystals, soluble in 3 parts of cold water. (Thénard, *Scher. J.* 10, 428.)

Nickel and Potassium.

A. Niccolate of Potash.—*a.* Hydrate of potash forms a bluish glass with oxide of nickel. (Kirwan.)—*b.* Aqueous potash solution added to niccolate of ammonia forms a green precipitate, which, when treated with hot water, gradually gives up all its potash and is converted into hydrated nickel-oxide. (Berzelius.)—*c.* Caustic potash dissolves an extremely small quantity of hydrated nickel-oxide. (Tupputi.)

B. Sulphate of Nickel-oxide and Potash.—Formed by mixing sulphate of nickel-oxide with sulphate of potash, or by dissolving nickel-oxide or its carbonate in aqueous bisulphate of potash.—Yellow when anhydrous. At a low red heat, it fuses to a brown liquid, which, if thrown into water when cold, diffuses itself through the water in the form of a yellow powder, and gradually dissolves. (Gm.) At a higher temperature it is converted into a black mixture, of nickel-oxide and sulphate of potash. In a moist atmosphere, it turns green, and in combination with water forms bluish-green, transparent, permanent crystals, of specific gravity 2·124 (Kopp), and isomorphous with sulphate of magnesia and ammonia, &c. (Mitscherlich.) *Fig.* 85; $i:u$ or $u'=102° 15'$; $i:a=154° 32'$; $i:f=116° 17'$; $u:u'=109° 10'$; $u:t=125° 25'$. (Brooke, *Ann. Phil.* 22, 438.) Soluble in 8 or 9 parts of cold water. (Tupputi.)

Nickel, Barium, and Strontium.

Niccolate of Baryta and Niccolate of Strontia.—Precipitated on mixing niccolate of ammonia with baryta- or strontia-water. Decomposed by sulphate of potash or sulphate of ammonia.

Nickel and Calcium.

Niccolate of Lime.—Similar to the baryta-compound.

Nickel and Magnesium.

Niccolate of Magnesia.—Precipitated on adding ammonia to a nickel-salt mixed with a magnesia-salt; excess of ammonia does not extract the whole of the nickel-oxide. (Berzelius.)

B. Phosphate of Nickel-oxide and Magnesia.—Precipitated on adding ammonia—even in excess—to an acid solution of nickel-oxide and magnesia containing phosphoric acid. (H. Rose.)

Nickel and Aluminum.

A. Aluminate of Nickel-oxide.—Analogous to the compound of nickel-oxide and magnesia.

B. Fluoride of Aluminum and Nickel, or Hydrofluate of Alumina and Nickel-oxide.—Formed by evaporating a mixed aqueous solution of hydrofluate of alumina and hydrofluate of nickel-oxide. Long, pale apple-green needles, which dissolve in water slowly but completely. Ammonia precipitates the salt A from the solution. (Berzelius.)

Nickel and Silicium.

A. Hydrated Fluoride of Silicium and Nickel, or Hydrofluate of Silica and Nickel-oxide.—NiF, SiF^2+7Aq. By evaporating a solution of nickel-carbonate in hydrofluosilicic acid. Green rhombohedrons and six-sided prisms easily soluble in water. (Berzelius, *Pogg.* 1, 198.)

B. Glass fluxes containing Nickel.—Oxide of nickel imparts a bluish colour to glass-fluxes containing potash and a hyacinth colour to those which contain soda.

Nickel and Tungsten.

A. Tungstate of Nickel-oxide. — *a. Monotungstate.* — Monotungstate of potash added to nickel-salts, throws down a light green powder, which gives off its water and turns yellow when ignited; in the unignited state, it is insoluble in water and oxalic acid, but dissolves in *boiling* phosphoric or acetic acid, and in warm ammonia. (Anthon.)

	Ignited.		Anthon.		*Dried in the air.*		Anthon.
NiO	37·5	23·81	25	NiO	37·5	17·73	18
WO^3	120·0	76·19	75	WO^3	120·0	56·74	54
				6HO	54·0	25·53	28
NiO,WO^3	157·5	100·00	100	+6Aq.	211·5	100·00	100

b. Bitungstate.—Alkaline bitungstates form with nickel-salts, a precipitate, which, when ignited, collects into a somewhat pasty mass; and this, on exposure to the air, hardens, becomes light green, and somewhat translucent. The light green powder which it yields, again becomes somewhat doughy when soaked in water. At a heat below redness, the mass turns brown and gives off its water; when strongly ignited it bakes together slightly. The unignited salt is insoluble in water, slightly soluble in oxalic acid, perfectly soluble in phosphoric or acetic acid.

	Ignited.		Anthon.		*Dried in the air.*		Anthon.
NiO	37·5	13·51	12·5	NiO	37·5	11·96	11
WO^3	240·0	86·49	87·5	$2WO^3$	240·0	76·56	77
				4HO	36·0	11·48	12
$NiO,2WO^3$	277·5	100·00	100·0	+4Aq.	313·5	100·00	100

B. Sulphotungstate of Nickel.—NiS,WS^3.—Similar to the cobalt-compound.

Nickel and Molybdenum.

A. Molybdate of Nickel-oxide.—Molybdate of potash forms with chloride of nickel, a light apple-green precipitate (Richter)—white, according to Hatchett,—slightly soluble in boiling water.

B. Sulphomolybdate of Nickel.—NiS,MoS^3.—Analogous to the cobalt-compound.

C. Persulphomolybdate of Nickel.—NiS,MoS^4.—Black-brown precipitate retaining the same colour when dry, soluble in excess of sulphomolybdate of potassium, but separating out again in the course of 24 hours. (Berzelius.)

Nickel and Vanadium.

Vanadiate of Nickel-oxide.—*a. Monovanadiate.*—The aqueous solution yields on evaporation a deep yellow, non-crystalline mass, which dissolves in water, but is precipitated from the solution on the addition of alcohol: the precipitate thus formed is yellow.—*b. Acid.*—The solution yields on evaporation small, deep yellow crystals, soluble in water, but precipitated again from the solution by alcohol. The solution in ammonia does not exhibit any blue colour. (Berzelius.)

Nickel and Chromium.

Chromate of Nickel-oxide.—*a. Monochromate?*—1. Formed by mixing the solution of *b* with a small quantity of fixed alkali, or digesting it with carbonate of nickel-oxide.—Reddish yellow powder, insoluble in water. (Tupputi.)—2. Chromate of potash mixed with sulphate of

nickel-oxide, forms an abundant precipitate on the application of heat: the liquid contains sulphate of nickel-oxide and potash. (Stokes, *Kastn. Arch.* 13, 191.)

b. Acid Chromate?—Aqueous chromic acid dissolves the hydrate or carbonate of nickel-oxide, forming a yellowish-red solution, which deposits a powder soluble in a larger quantity of the acid; and the latter solution deposits, according to Tupputi, a non-deliquescent crystalline mass,—according to John, red crystals aggregated in fern-like tufts. The dry residue is resolved at a red heat into chromic-oxide and nickel-oxide. (John.)

Permanganate of potash gives no precipitate with chloride of nickel. (Fromherz.)

Nickel and Arsenic.

A. Arsenide of Nickel.—*a.* A very small quantity of arsenic is sufficient to render nickel fusible before the blowpipe under borax; the nickel, however, when thus alloyed, retains its ductility and magnetic power. (Berzelius.)

b. With 4 At. Arsenic?—α. 100 parts of finely-divided nickel, heated in a close vessel with 200 arsenic, form, without visible combustion, from 150 to 156 parts of pulverulent or brittle arsenide of nickel. (Gehlen.)—β. 100 parts of arseniate of nickel-oxide heated to whiteness in a charcoal crucible, yield 61·5 parts of arsenide of nickel, having the form of a greyish-white, brittle, non-magnetic button, exhibiting a fine-grained texture, and containing about half as much arsenic as copper-nickel. (Berthier.)

γ. *Placodine.*—Crystalline system the oblique prismatic. The form is that of *figures* 91 to 120, with the faces u, t, i, and f united; the faces e and z are likewise present in some crystals, $u : u' = 64° 32'$; $t : u = 122° 16'$; $t : z = 133° 28'$; $t : f = 120° 5'$; cleavage parallel to u and t. Specific gravity from 7·988 to 8·062. Bronze-yellow, somewhat lighter than magnetic pyrites; yields a black powder. (Breithaupt, *Pogg.* 53, 631.) —When heated in a tube, it gives off arsenious acid, and likewise sulphurous acid if a strong current of air plays over it. Before the blowpipe on charcoal, it fuses with tolerable facility, and emits arsenical fumes; after roasting, it yields a blue glass with borax. (Plattner, *Pogg.* 58, 283.)

	Placodine.				Plattner.
4Ni	117	....	60·94	.....	57·05
Co		....		.....	0·92
Fe		....		.....	trace
Cu		....		.....	0·86
1As	75	....	39·06	.....	39·71
S		....		.....	0·62
Ni^4As	192	....	100·00	.....	99·16

c. Trisarsenide.—Crystallized Cobalt-speiss.—Found on taking down a worn-out blue-colour furnace. More rarely found in cobalt-speiss run out from the glass-pots. Appears to be produced by long-continued fusion of copper-nickel contained in cobalt-ores. (Wöhler.)—Crystalline system the square prismatic. *Fig.* 24 and 35; $p : e = 122° 10'$; $e : e' = 106° 28'$ $e : e'' = 115° 39'$; $e : \epsilon = 105° 17'$; $\epsilon : \epsilon'' = 145° 5'$. Cleavage nes imperceptible. Fracture uneven. (G. Rose, *Pogg.* 28, 434.) Has

a strong lustre and a light pinchbeck-colour, less red than copper-nickel. Not magnetic. (Wöhler, *Pogg.* 25, 302.)

Crystallized.		*Cobalt speiss.*		Wöhler.
3Ni	88·5	54·13		52·70
As	75·0	45·87		44·05
Mn, Fe, Cu				1·60
S				1·65
Ni^3, As	163·5	100·00		100·00

d. Di-arsenide.—Copper-nickel.—Double six-sided pyramid. (Glocker, *J. pr. Chem.* 12, 182.) Crystalline system the right prismatic; *Fig.* 48, without the *p*-face, and without the truncation between *u* and *a*; $i : i = 60° 16'$; $i : a = 133° 25'$. (Breithaupt, *Schw.* 68, 445.) Sp. gr. from 7·5 to 7·65. Harder than apatite; emits an arsenical odour when struck with steel. Fracture conchoidal. Colour copper-red; powder brownish-black. Non-magnetic. When heated in a glass tube, it fuses just when the glass begins to soften, giving off arsenious acid but no free arsenic. On charcoal before the blowpipe, it emits a strong arsenical fume, and fuses into a silver-white, brittle button. When roasted in the air, it leaves a yellow-green residue, which, when fused upon charcoal with carbonate of soda and a little borax, yields a tolerably ductile, magnetic button of metal. (Berzelius.) When heated to whiteness for an hour, it loses from 12 to 15 per cent. in weight, but without alteration of appearance. (Berthier.) Enclosed in a charcoal crucible, and heated for half an hour in the blast-furnace, it gives off 4 per cent. of arsenic. (Wöhler.)—Dissolves in nitric acid with separation of arsenious acid, more readily in aqua-regia.

	At.	*Copper-nickel.*		Stromeyer. Ricchelsdorf.	Suckow.*	Schnabel.† Westphalia.
Ni	2	59	44·03	44·21	45·76	45·37
Co						
Fe				0·34	2·70	
Pb				0·32		Cu 1·44
Sb						
As	1	75	55·97	54·73	53·69	52·71
S				0·40	0·15	0·48
Ni^2, As		134	100·00	100·00	102·30	100·00

	At.	*Copper-nickel.*		Berthier. Allemont.	At.	*Copper-nickel.*		Berthier. Balen.
Ni	24	708	42·60	39·94	6	177	38·82	33·67
Co				0·16				
Fe				& Mn trace				1·43
Sb	1	129	7·76	8·00	1	129	28·29	28·37
As	11	825	49·64	48·80	2	150	32·89	33·67
S				2·00				2·86
		1662	100·00	98·90		456	100·00	100·00

In the varieties examined by Berthier, part of the arsenic is replaced by antimony: he supposes that the sulphur is in the state of sulphide of antimony.

e. Mono-arsenide.—Arsenical Nickel or *White Nickel-pyrites* (*Weiss-nickelkies*) of mineralogists. Cubes with the faces of the octohedron and

* Verwitterung in Mineralreich, I., Heft. p. 68.
† Rammelsberg's *Handw.*, 4 Suppl. p. 122.

dodecahedron; or a fine-grained mass. (Booth, *Sill. Am. J.* 29, 241; also *Pogg.* 32, 295.) Sp. gr. 6·735. (Rammelsberg.) Harder than apatite; brittle; tin-white. Before the blowpipe it behaves like copper-nickel, but when heated in a glass tube closed at one end, it yields a sublimate of arsenic and a copper-coloured residue of arsenide of nickel. (Berzelius.)

	At.				Rammelsberg.	Booth.	Hofmann.	Rammelsberg.*
					Riechelsdorf.		Schneeberg.	Allemont.
Ni	1	29·5	28·23		28·95	20·74	28·14	18·71
Co	—	—	—			3·37		
Fe	—	—	—		trace	3·25		6·82
Cu	—	—	—			—	0·50	
Bi	—	—	—			—	2·19	
As	1	75·0	71·77		70·64	72·64	71·30	71·11
S	—	—	—			—	0·14	2·29
		104·5	100·00		99·59	100·00	102·27	98·93

B. Arsenite of Nickel-oxide, or Nickel-arsenite.—Formed by mixing arsenite of potash with a dissolved nickel-salt.—Apple-green powder, which, when ignited in a glass tube, gives off water and arsenious acid, but not all that it contains, becoming first blackish, then olive-green (light green, according to Berzelius). On igniting the salt in a platinum crucible, the arsenious acid quickly volatilizes, and pure nickel-oxide remains behind.—Insoluble in water, but easily soluble in ammonia. (Proust.)

C. Arseniate of Nickel-oxide, or Nickel-arseniate.—*Terbasic.* Double decomposition yields an apple-green powder, or apple-green crystalline grains having a metallic taste.—Arseniate of nickel-oxide heated not in contact with carbonaceous matter, gives off nothing but water, becoming at first hyacinth-coloured and transparent, and assuming a light yellow colour when ignited; at higher temperatures, it exhibits no further alteration, unless it comes in contact with combustible matter. (Proust.) When heated with sulphur, it gives off sulphurous acid, and first yellow, then red sulphide of arsenic, and leaves sulphide of nickel. (Döbereiner.) Gives up its acid to fused hydrate of potash.—Insoluble in water, soluble in arsenic acid, and in the stronger mineral acids. Easily soluble in aqueous ammonia. Potash added to the ammoniacal solution precipitates niccolate of potash free from arsenic, unless ferric oxide is present, in which case the precipitate likewise contains arsenic acid. (Berzelius.) On dissolving it in an acid cobalt-salt, and adding a small quantity of potash, arseniate of cobalt-oxide is precipitated.

Nickel-ochre or *Nickel-bloom* is also a trisarseniate of nickel-oxide. It is produced by oxidation of arsenide and sulpharseniate of nickel, which takes place more quickly than with the corresponding cobalt-ores. The most oxidable of all is the white nickel-pyrites, which quickly tarnishes and blackens when immersed in aerated water, and after a few months exhibits apple-green spots on its projecting points; next in order of oxidability is copper-nickel, and lastly nickel-glance. Together with nickel-ochre, which is never crystalline, this weathering process sometimes produces crystalline needles consisting of sulphate of nickel-oxide and sulphate of lime. The green coating with which the three ores above

* Rammelsberg's *Handwörterbuch*, 4 Suppl. p. 8.

mentioned become covered by exposure to damp air, contains nickel-ochre mixed with arsenious acid: in the mines, the arsenious acid is dissolved out by water. (Karsten, *Pogg.* 60, 267.)—Nickel-ochre is massive, earthy, friable, apple-green, and greenish-white. When ignited in a retort, it gives off water, which sometimes reddens litmus from admixture of sulphuric acid; in the latter case, it often likewise yields a sublimate of arsenious acid; the residue is yellow. (Karsten.) Heated on charcoal before the blowpipe, it gives off a strong fume of arsenic, and fuses in the inner flame to a metallic button containing arsenic. Water extracts from it traces of sulphuric acid, frequently also of the sulphates of nickel-oxide, cobalt-oxide, and lime. (Karsten.) Dissolves readily in hydrochloric or nitric acid.

	At.			Stromeyer. a.	Berthier. b.	c.	d.	e.
NiO	3	112·5	37·56	37·35	36·2	36·20	35·00	36·10
CoO					2·5	1·53		trace
Fe^2O^3				1·13		trace	2·21	1·10
AsO^5	1	115·0	38·40	36·97	36·8	38·30	38·90	37·21
HO	8	72·0	24·04	24·32	24·5	23·91	24·02	23·92
AsO^3								0·52
SO^3				0·23				
CaO, SO^3						trace		trace
CoO, SO^3							trace	
$3NiO, AsO^5 + 8Aq.$		299·5	100·00	100·00	100·0	99·94	100·13	98·85

a. From Riechelsdorf.—*b.* from Allemont.—*c.* from a mine near Schneeberg. Gives off slightly acidulated water when ignited, but no arsenious acid.—*d.* From the *Adam Haber-Fundgrube,* near Schneeberg. Gives off water containing a trace of sulphuric acid.—*e.* From the *Weisser Hirsch* mine, near Schneeberg. Yields a slight sublimate of arsenious acid.

D. Bisulphide of Nickel with Proto-arsenide of Nickel.—*Nickel-glance* or *Nickel-arsenic-glance.*—Octohedrons, sometimes with the faces of the pentagonal dodecahedron and cubo-octohedron. Cleavage parallel to the cube-faces. Sp. gr. 6·097 (G. Rose); from 6·238 to 6·331 (Breithaupt); 6·757 (Mohs); from 6·7 to 6·9 (Hörner). Harder than apatite. Tin-white inclining to lead-grey; yields a greyish-black powder.—Decrepitates strongly when heated in a flask, and when heated to redness yields a strong sublimate of fused, yellowish-brown sulphide of arsenic, while a mass like copper-nickel is left behind. (Berzelius.) Dissolves in nitric acid, with separation of sulphur and arsenious acid.

	At.	*Nickel-glance.*		Berzelius. Loos.	Döbereiner. Kamsdorf.	Rammelsberg. Haueisen.	Hörner. Schladming.
Ni	2	59	35·54	29·94	27	31·82	38·42
Co + Cu				0·92			trace
Fe				4·11	11		2·09
As	1	75	45·18	45·37	48	48·02	42·52
S	2	32	19·28	19·34	14	20·16	14·22
Quartz				0·90			1·87
$NiAs, NiS^2$		166	100·00	100·58	100	100·00	99·12

	Löwe.*				Schnabel.†
	Schladming.		Prakendorf.		Müsen.
Ni	26·14	....	28·75	....	32·66
Fe	9·55	....	8·90	....	2·38
As	49·83	....	46·10	....	46·02
S	14·13	....	16·25	....	18·94
	99·65	....	100·00	....	100·00

Of the two varieties examined by Löwe, that from Schladming was crystallized, that from Prakendorf was massive; the variety analyzed by Schnabel was crystallized.

E. Sulpharsenite of Nickel.—$2NiS,AsS^3$.—Black precipitate, which remains black on drying and yields a black powder; when distilled, it yields orpiment and leaves a residue of yellow, coagulated sulphide of nickel. (Berzelius.)

F. Sulpharseniate of Nickel.—$3NiS,AsS^5$, and $2NiS,AsS^5$.—Both bibasic and terbasic sulpharseniate of sodium produce with dilute nickel-salts, a clear, yellowish-brown liquid, which gradually darkens and forms a precipitate; in a concentrated solution, the precipitate is formed immediately. It is dark brown at first, but becomes black when collected and dried; it is not decomposed by hydrochloric acid, but dissolves in an excess of the aqueous sodium-salt. When arseniate of nickel-oxide dissolved in hydrochloric acid is precipitated by hydrosulphate of ammonia in excess, the precipitate contains sulpharseniate of nickel, together with sulphide of nickel. (Berzelius.)

Nickel and Antimony.

A. Antimonide of Nickel.—*Di-antimonide.*—1 part of nickel powder, heated with 2 parts of antimony powder, produces a blackish-grey, metallic powder, the combination being attended with the emission of a red light. (Gehlen.)—On fusing together 1 At. (59 parts) of nickel with 1 At. (129 parts) of antimony, light and heat are emitted, and a magnetic mass is obtained exactly resembling the following native compound in hardness, lustre, and colour, and likewise in its behaviour with heat and with acids. (Stromeyer, *Schw.* 69, 252; also *Pogg.* 31, 134.)

Antimonial Nickel (*Antimonnickel*, or *Antimonnickelerz*) of mineralogists. Obtuse, double six-sided pyramid, *Fig.* 131; *length of the principal axes* : *length of the secondary axes* = 1·3. Sp. gr. 7·541 (Breithaupt, *Pogg.* 51, 512). Six-sided tables; fracture uneven; harder than fluorspar; the recent fracture exhibits a light copper-colour with a tinge of violet; powder red-brown. Not magnetic. When ignited in a glass tube, it yields a small sublimate of antimony. On charcoal it forms an antimonial deposit, and cannot be fused excepting in very small pieces. But little attacked by simple acids; dissolves easily—and completely if no galena is mixed with it—in aqua-regia. (Stromeyer & Hausmann.)

* *Jahresb.* L. & K. 1847–8, 1155.
† *Ibid.* ,, 1849, 720.

					Stromeyer. Andreasberg.
	Antimonial Nickel.				
2Ni	59	....	31·38	.....	30·93
Fe		....		.....	0·89
1Sb	129	....	68·62	.....	68·18
Ni^2,Sb	188	....	100·00	.....	100·00

B. Antimoniate of Nickel-oxide.—Greenish-white, insoluble in water. (Berzelius.)

C. Bisulphide of Nickel with Antimonide of Nickel.—*Nickeliferous grey Antimony, Hartmannite* (*Nickelspeissglanzerz* or *Nickelantimonglanz*).—Regular octohedrons with the faces of the cube and rhombic dodecahedron. Cleavage parallel to the cube-faces. Specific gravity 6·45; harder than fluorspar. Fracture fine-grained. Colour lead-grey inclining to steel-grey; powder greyish-black. Before the blowpipe on charcoal, it emits a strong antimonial fume, together with sulphurous acid, and sometimes with a very slight arsenical fume, and fuses into a metallic globule, which remains brittle and fusible even after long blowing; and if fused with carbonate of soda, does not sink into the charcoal, but forms a black bead containing sulphide of sodium. (Berzelius.) The mineral dissolves in nitric acid with separation of antimonic nitrate, and in aqua-regia with separation of sulphur.

					H. Rose. Landskrone.		John. Sayn-Altenkirchen.		Klaproth. Frensburg.
	Nickeliferous grey Antimony.								
2Ni	59	....	26·82	.....	27·36	....	23·33	....	25·25
1Sb	129	....	58·64	.....	55·76	....	61·68	....	47·75
As		....		.....		....		....	11·75
2S	32	....	14·54	.....	15·98	....	14·16	....	15·25
$NiSb,NiS^2$	220	....	100·00	.....	99·10	....	99·17	....	100·00

In the ore examined by Klaproth, part of the antimony is replaced by arsenic, whereby a transformation into the isomorphous mineral, *Nickel-glance*, is produced.

D. Sulphantimoniate of Nickel.—$3NiS,SbS^5$.—Precipitated on mixing an aqueous nickel-salt in any proportion whatever, with Schlippe's salt.—Black; oxidates in the air; decomposed by heated hydrochloric acid. (Rammelsberg, *Pogg.* 52, 236.)

Nickel and Tellurium.

A. Tellurite of Nickel-oxide.—Formed by double decomposition. Very pale greenish-white flakes.

B. Tellurite of Nickel-oxide. Exactly similar. (Berzelius.)

C. Sulphotellurite of Nickel.—Black precipitate. (Berzelius.)

Nickel and Bismuth.

A. Bismuth-nickel.—Brittle, laminar alloy. (Cronstedt.)

B. Sulphide of Bismuth and Nickel.—*Nickel-bismuth-glance.*—Octohedrons and cubo octohedrons, with cleavage-planes parallel to the

octohedral faces. Harder than apatite. Colour steel-grey, inclining to silver-white; powder grey. Fuses readily before the blowpipe, emitting an odour of sulphurous acid, and under the action of a long-continued blast, covers the charcoal with a yellowish deposit, and yields a strongly magnetic grey bead, bronze-yellow on the fractured surface. With borax or microcosmic salt, it yields a brown glass in the outer flame. Dissolves readily in strong sulphuric acid, with separation of sulphur; gives off sulphuretted hydrogen when treated with hot hydrochloric acid; not decomposed by caustic potash.

Nickel-bismuth-glance, from Sayn-Altenkirchen (Kobell.)

Fe	3·48
Co	0·28
Ni	40·65
Cu	1·68
Pb	1·58
Bi	14·11
S	38·46
	100·24

Nickel and Zinc.

Nickel-Zinc.—1 part of nickel powder unites with 2 parts of zinc-foil, emitting a red light, and forming a blackish-violet powder and brittle metallic globules. (Gehlen.) The combination is attended with combustion and explosion. (Gersdorff, *Pogg*, 8, 103.)

B. Sulphate of Nickel-oxide and Zinc-oxide.—Zinc dissolves, with evolution of hydrogen, in aqueous nickel-sulphate containing excess of acid. The solution yields pale green crystals resembling the rhombic crystals of nickel-sulphate; they have a sharp, astringent, and metallic taste, effloresce with ease to a white powder, and dissolve in 3 or 4 parts of cold water. (Tupputi.)

Nickel and Tin.

Nickel-Tin.—White, hard, brittle alloy.

Nickel and Lead.

A. Nickel-Lead.—The two metals may, with some difficulty, be made to unite and form a grey, slightly lustrous, laminar and friable alloy. (Cronstedt, Tupputi.)

B. Plumbite of Nickel-oxide.—Analogous to niccolate of magnesia.

Nickel and Iron.

Alloys of Nickel and Iron.—Combination takes place with ease.

a. 3 parts Nickel to 2 Iron: Grey, moderately hard, perfectly malleable alloy, whose magnetic power is to that of iron as 35 : 55. *(Lampadius.)*

b. 1 pt. Nickel to 10 Iron: Greyish-white inclining to yellow, less malleable, and less inclined to rust than pure iron. Sp. gr. 7·849.

c. 1 pt. Nickel to 33 Iron: Somewhat whiter than iron, and less inclined to rust, but equally malleable. Sp. gr. 7·804. (Faraday & Stoddart, *Gilb.* 66, 289.)

Meteoric Iron also is principally an alloy of iron and nickel. The following are analyses of various specimens:

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Mg	....	....	....	0·05	....	....	....	0·28
Cr	3·24							
Mn	....	....	0·2	0·13	....	....	....	trace
Fe	66·56	85·61	81·8	88·04	90·02	90·24	89·78	88·23
Co	....	0·89	1·0	0·46	....	....	0·67	0·76
Ni	24·71	12·28	11·9	10·73	9·68	9·76	8·89	
Cu	....	....	....	0·07	....	....	....	8·52
Sn	....	....	....		....	....		
C	....	....	....	0·04				
S	4·00	....	5·1	trace	....	....	....	trace
Cl	1·48							
Insol.	....	....	....	0·48	....	....	....	2·21
	99·99	98·78	100·0	100·00	99·70	100·00	99·34	100·00

a. From Clairborne, in Alabama. (Jackson.)

b. From Cap; sp. gr, 7·665. (Wehrle.)

c. From Rittburg (Stromeyer); had been previously fused at the forge. Fragments of the unfused mass have, according to Steininger, a density of 6·14.

d. The Pallas meteoric iron from Siberia (Berzelius). The word *Insol.* denotes the portion insoluble in hydrochloric acid, the analysis of which is given below.

e. From Louisiana. (Shepard.)

f. From Potosi. (Morren.)

g. From Hraschina near Agram; sp. gr. 7·78. (Wehrle.)

h. Metallic mass "*des verwünschten Burggrafen*" in Elbogen. (Berzelius.)

	i.	*k.*	*l.*	*m.*	*n.*	*o.*	*p.*	*q, a.*	*q, β.*
MgO	....	....	....	....	....	....	....	2·10	2·0
Cr	....	....	....	....	....	....	....	0·50	
Fe	89·12	91·23	93·57	....	93·78	88·36	96·75	87·35	91·5
Co	0·66	....	0·53	....	0·21	trace			
Ni	8·26	8·21	6·62	4·61	3·81	4·80	3·25	2·50	1·5
Cu	trace								
Sn									
C									
S	....	....	....	....	....	6·83	....	1·85	1·0
Insol.	....	0·28	....	....	2·20	....	....	SiO^2 6·30	3·0
	98·04	99·72	100·72		100·00	99·99	100·00	100·60	99·0

i. From Lenarto; sp. gr. 7·798. (Wehrle.)

k. From Tokavito in Columbia. (Boussingault.)

l. From Atacama. (Turner.)

m. From the eastern shore of the Great Fish River. (Herschel.)

n. From Bohumilitz in Bohemia; *Insol.* denotes the portion insoluble in nitric acid.

o. Metallic particles extracted by the magnet from the meteoric iron from Macedonia, containing magnetic pyrites together with nickel-iron.

p. From Durango in Mexico. (Klaproth.)

q. From Brabin in Poland. *α.* Bluish variety; *β.* white. (Laugier.)

The specimens of meteoric iron from Cap, Agram, Bittburg, Lenarto, Gotha, and Elbogen, and likewise those from Brazil, Buenos Ayres, Lousiana, and Siberia, contain from 0·1 to 0·2 per cent. of copper. (Stromeyer.)

Composition of the residues insoluble in acids:

	a.		*b.*		*c.*
Mg	9·66	....	17·72	....	15·01
Ni	18·33				
Fe	48·67	....	68·11	....	65·99
Cu and Sn	trace				
Si		....		....	2·04
P	18·47	....	14·17	....	14·02
C and loss	4·87	....		C	1·42
	100·00	....	100·00	....	98·48

a. The residue left on dissolving the Pallas iron from Siberia in dilute hydrochloric acid.—*b.* The same from the Elbogen iron.—*c.* When the meteoric iron from Bohumilitz is dissolved in dilute nitric acid, an insoluble residue is left, amounting to between 2·20 and 2·26 per cent.; it consists of about equal parts of white, metal-shining scales, whose composition is given under *c*, and a carbonaceous substance, after the combustion of which there remains a small quantity of basic phosphate of ferric oxide, together with nickel-oxide, silica, and a trace of chrome-iron-ore. These insoluble phosphorus-compounds appear to be the cause of the crystalline figures (*Wiedmanstädt's figures*) which are developed when a bright surface of meteoric iron is etched with acids. (Berzelius.)

For other analyses of meteoric iron, vid. *Jahresber, L. & K.*; 1847–8, p. 1298; 1849, p. 827.

B. and C. Niccolate of Ferrous Oxide, and Ferrite of Nickel-Oxide.—Analogous to niccolate of magnesia.

D. Carbide of Nickel and Iron.—1 part of nickel forms with 8 or 10 parts of steel, a damask-figured alloy, which has a density of 7·684, and rusts much more quickly than pure steel. (Faraday & Stoddart.)

F. Sulphide of Nickel and Iron.—*Iron-nickel Pyrites* (*Eisen-nickelkies*).—Crystalline masses, with cleavage-planes parallel to the faces of a regular octohedron. Sp. gr. 4·6. Hardness equal to that of magnetic-pyrites. Colour light bronze-brown; lustre faintly metallic. Not magnetic. The pulverized ore was freed from magnetic-pyrites by the magnet, previous to analysis; it is likewise mixed with copper-pyrites,—hence the copper. (Th. Scheerer, *Pogg.* 58, 315.)

Iron-nickel pyrites.

2Fe	56·0	....	41·95	.....	40·21
1Ni	29·5	....	22·10	.....	21·07
Cu		....		.....	1·78
3S	48·0	....	35·95	.....	36·64
2FeS,NiS	133·5	....	100·00	.....	99·70

F. Sulphate of Nickel-oxide and Ferrous Oxide.—Forms with water, green rhombic crystals, which crumble to a yellow powder when exposed to the air. (Link. *Crell. Ann.* 1796, 1, 31.)

Nickel and Cobalt.

Nickel-cobalt.—The two metals easily fuse together.

Other Compounds of Nickel.

With Copper, Mercury, Silver, Gold, Platinum, and Palladium.

Chapter XXXV.

COPPER.

Proust on Copper. *Ann. Chim.* 32, 26; also *Crell. Ann.* 1800, 1, 39.—*J. Phys.* 51, 173; also *Scher. J.* 8, 290.—*J. Phys.* 53, 89; also *Scher. J.* 9, 388; also *Gilb.* 25, 164.—*J. Phys.* 59, 393; also *A. Gehl.* 6, 552.—*J. Phys.* 79, 126.
Karsten. *System der Metallurgie*, 5, 231; also *Schw.* 66, 255.
Kane. Ammoniacal compounds of Copper. *Ann. Chim. Phys.* 72, 265.

Synonymes. *Cuivre, Kupfer, Cuprum, Venus.*

History.—Known from the earliest times; the name is derived from that of the island of Cyprus. Many of its compounds have been most exactly investigated by Proust.

Sources.—As native copper. ¶ Large masses of native copper have been found on the coast of Lake Superior in North America. Forrest Shepherd (Sill. *Am. J.* [2], 4, 115) describes a mass found on the south coast of that lake, near the mouth of the river Elm, which was 3½ feet long, 2½ feet broad, between 7 and 8 inches thick, and weighed 1625 pounds. Its surface exhibited specks of metallic silver, and particles of syenite and sandstone were found in its cavities. It appeared to have been transported from a bed of greenstone situated eight or nine miles to the southward, in which masses of native copper are found, likewise dotted with silver. Another mass previously found in the same locality weighed 2200 pounds. A third mass weighing 110 pounds is mentioned by Cordier (*Compt. rend.* 28, 161) as likewise coming from the shores of

water from mines, in which cupric sulphate is produced by the weathering of ores containing sulphide of copper, and likewise to the ley obtained by roasting ores of this nature and exhausting the product with water.

a. is Swedish copper (*Scheiben-kupfer*).—*b.* from Mansfeld (*v.* Kobell, *J. pr. Chem.* 1, 372).—*c.* Copper from Switzerland, distinguished by peculiar softness and malleability, partly attributable perhaps to the potassium which it contains. (Berthier, *Ann. Chim. Phys.* 44, 120.) *d.* Native copper from Brazil, sp. gr. 8·962. (Marchand & Scheerer, *J. pr. Chem.* 27, 193.)

	a.		*b.*		*c.*		*d.*
Cu	98·655	....	98·251	....		....	99·56
Fe	0·055	....	0·131	....	0·17	....	0·10
Ni		....	0·236			....	
Pb	0·751	....	1·092	....		Au	0·08
Ag	0·226	....	0·135	....		....	0·30
K	0·116	....		....	0·38		
Ca	0·095	....	0·107	....	0·33		
Mg	0·033						
Al	0·021	....	0·048				
Si	0·048						
	100·00	....	100·000	....		....	100·04

[For analyses of copper containing nickel, *vid. Jahresber. L. & K.* 1847–8, 1038.]

Karsten never found sulphur in toughened copper.—The Japanese copper is nearly pure; other kinds, which are less pure, may be freed from the other ignoble metals, by ignition for half-an-hour with one-third of their weight of nitre in a covered Hessian crucible. (Lampadius.) ¶ Percy (*Chem. Gaz.* 1849, 47) has examined copper mixed with phosphorus by fusion; he found in two specimens, 0·93 and 2·41 phosphorus together with 1·99 and 2·41 iron (arising from stirring the fused metal with an iron rod). The copper thus alloyed was distinguished by peculiar hardness, and its malleability, though less than that of ordinary copper, was not impaired to a degree corresponding to the increase of hardness. ¶

Properties.—The crystals of native copper, and likewise those obtained by fusion, belong to the regular system, *Fig.* 1, 2, 3, 4, 5, 8, and 11. Hauy likewise found native copper in the form of *Fig.* 138, and Seebeck found in Hermbstädt's collection, artificial crystals apparently belonging to the rhomboidal system. It has, however, been shown by Haidinger and G. Rose (*Pogg.* 23, 197; 55, 331), that these forms are macled crystals of the pyramidal cube, and therefore belong, like the others, to the regular system.—When a dilute solution of copper is left for some time in contact with wood, the copper is sometimes deposited from the liquid in cubes, octohedrons, and long four-sided prisms (elongated cubes) acuminated with 4 (octohedral) faces resting on the edges. (Wagner, *Schw.* 47, 325.) In other cases, the wood precipitates the copper in thin ductile plates with warty surfaces. (Clement, *Ann. Chim. Phys.* 27, 440; also *Schw.* 44, 86; Bischof, *Pogg.* 3, 195.) Copper in the massive state, is very hard and elastic and strongly sonorous; it has considerable toughness, may be beaten out into very thin leaves, and drawn out into very fine wire; its fracture is red, shining, indented, and slightly granular; after hammering, it exhibits a sinewy fracture, with a light-red, silky radiance. The greater the purity of copper, the greater is its malleability and, generally speaking, its softness, and the less heat does it require to

deprive it of the brittleness produced by beating. Copper contaminated with other metals exhibits, not an indented, but a scaly, granular fracture with but little lustre, and after hammering, a scaly, dingy-red fracture, also with but feeble lustre. (Karsten.) For the effect of particular impurities, *vid.* Copper and Carbon; Cu. and Potassium; Cu. and Arsenic; Cu. and Antimony; Cu. and Bismuth; Cu. and Zinc; Cu. and Tin; Cu. and Lead; Cu. and Iron. Sp. gr. of native crystallized copper, 8·94; of copper precipitated by the electrotype process, 8·914; of pure copper after fusion, 8·921; of unignited copper wire, from 8·939 to 8·949; of ignited wire, 8·930; of flattened wire, 8·951; of copper plate formed by rolling and afterwards hammered, 8·952, &c., &c. (Marchand and Scheerer, *J. pr. Chem.* 27, 193.)—Since copper in fusing takes up oxygen from the air, which it afterwards gives off on solidifying, it generally contains air-cavities within its substance, which diminish its specific gravity; and as these cavities are diminished in size by the subsequent hammering, rolling, or wire-drawing, the specific gravity of the copper is thereby increased. As this circumstance was formerly not sufficiently attended to, it was supposed that copper increased considerably in density by working (*vid. infra*). But copper fused under common salt, which prevents the absorption of oxygen from the air, has a density of 8·921, which, by a pressure of 300,000lbs. in the hydraulic press, is increased only to 8·930, an increase so slight, that it is probably due, not so much to an actual approximation of the atoms of the metal, as to the diminution of hollow spaces still remaining in it. (Scheerer & Marchand.)—Older determinations of the specific gravity of copper: Fused, 8·788; hammered 8·878 (Brisson); fused, 8·85; hammered, 8·95 (Berzelius); fused, 8·90 (Herepath); fused, 8·8969; after ignition and fusion with charcoal, 8·926; after fusion in the air, 8·6345 (Karsten). Copper is especially distinguished by its red colour.

In the finely-divided state, copper is a soft, dark-red, dull-looking powder, which, if pressed together while red hot, welds together into a compact mass.—Pulverulent copper is obtained: 1. By reducing the carbonate at a very gentle heat in an atmosphere of hydrogen. (Osann, *Pogg.* 52, 406.)—2. By boiling a concentrated solution of blue vitriol not containing free acid, with distilled zinc. As soon as the liquid loses its colour, which it does in a short time, the zinc is removed, and the copper powder well boiled with dilute sulphuric acid, then washed uninterruptedly with water, pressed between bibulous paper, and dried at 75°, or in a warm retort through the tubulure of which a stream of hydrogen is passed. (Böttger, *Ann. Pharm.* 39, 172.)—3. By igniting a mixture of 5 pts. dichloride of copper, and 6 dry carbonate of soda with sal-ammoniac, and afterwards exhausting with water. (Wöhler & Liebig, *Pogg.* 21, 582.)—Pulverulent copper, after being pressed together, may be welded in the same manner as platinum by Wollaston's method, with the precaution, however, of saturating it with oil before each ignition, to prevent the formation of oxide. (Fournet, *Ann. Chim. Phys.* 75, 435.) On this welding property of copper, is founded Osann's method of obtaining impressions in copper by pressure and ignition. (*Pogg.* 52, 406.)

Copper melts at 1207° (Guyton Morveau), at 1398° (Daniell), more easily than gold, less easily than silver, and in the fused state, exhibits a bluish-green colour. It expands in solidifying.—On the mirror-surface of melted copper, a number of dull stellate spots quickly form and disappear again, as long as it continues in the liquid state. (Karsten.)——Copper containing red oxide fuses more readily than pure copper, but

does not form so thin a liquid, flowing on the contrary in thicker streams, which solidify more slowly; the dull spots on the surface are larger, do not exhibit the same active movement, and go on increasing till the surface is solidified. If the proportion of red oxide is large, the mass does not expand in solidifying. An admixture of 0·1 per cent. of potassium, zinc, or lead, is likewise sufficient to prevent expansion in solidifying. Copper containing carbon behaves in the fused state like pure copper, but the motion of the spots, as they appear and disappear, is still more lively. (Karsten.)

Copper exposed to the air while in the melted state, absorbs a small quantity of oxygen, which escapes again as the metal solidifies, and sometimes makes the copper porous, sometimes, on sudden cooling, breaks through the crust already formed on the surface, and produces spitting or projection of the copper (*das Spritzen oder Spratzen des Kupfers*). This fact, first asserted by Lucas, and afterwards denied by Chevillot and Schweigger-Seidel (*Schw.* 53, 195), is established by the following observations: Copper kept in a state of fusion in the air, and then poured into water, produces violent detonations, an effect which is not produced if the copper be previously fused for half an hour under a layer of charcoal powder; in the former case, the copper is brittle [from the presence of red oxide?], in the latter, ductile. (Lucas, *Ann. Chim. Phys.* 12, 402.) Fearful explosions are likewise produced by pouring water on the surface of melted copper before it solidifies. Copper which spits after refining —in which case small granules of metal are thrown up to the height of 8 inches (Gilbert, *Gilb.* 37, 378)—is brittle, whereas that which does not spit is ductile. (Schweigger-Seidel.) — When copper spits, the hissing noise of the evolved gases is distinctly heard. (Marx, *Schw.* 55, 108.)— When copper is fused under a layer of common salt, it exhibits a smooth surface after solidification, and no hollow spaces when sawn through; but copper fused under a layer of fluorspar, or fluorspar with glass, borax with glass, or carbonate of soda with glass, exhibits vacant spaces close under the surface when sawn through, and warty elevations on the surface corresponding to these cavities; if it be slowly cooled after fusion, the cavities are less considerable, and consequently the specific gravity is higher, but still below the true specific gravity of the solid metal. Common salt forms a well-fused covering, which appears to prevent completely the access of air; but fluorspar, or a mixture of that substance with glass, does not fuse perfectly, and therefore does not prevent the contact of the air. When a mixture of borax or carbonate of soda with glass is used, it may be supposed that the copper takes oxygen from these compounds [or, perhaps, that these fluxes take up oxygen from the air and transfer it to the copper]. (Marchand & Scheerer, *J. pr. Chem.* 27, 105.)

Copper boils at an intense white heat, *e.g.*, before the oxy-hydrogen blowpipe.

Compounds of Copper.

Copper and Oxygen.

1. Copper in the massive state does not oxidate at ordinary temperatures in dry air, or even in damp air, unless carbonic acid is present. When heated to redness, its surface assumes a yellow, and then a violet *tint*, and afterwards becomes covered with a black crust, which consists

of protoxide without and dioxide within, and falls off in scales when the metal is suddenly cooled in water; *Scale-oxide of Copper*. Copper plate kept at a bright red heat for 4—7 hours in a muffle-tube, is for the most part converted merely into dioxide; it is only when the metal in the inner part has completely disappeared, that a larger proportion of protoxide is formed. (Anthon, *Repert.* 76, 216.) Finely-divided copper takes fire in the air at a temperature considerably below redness, and is converted into protoxide.—When copper is fused in the air in considerable quantities, large crystals of the dioxide are often formed. (Mitscherlich.) Copper kept at a white heat till it boils, burns with a light green flame, and is converted into protoxide: *Flowers of Copper, Flores Cupri.*—2. In contact with water and air containing carbonic acid, copper becomes tarnished, first with a blackish-grey, and then with a bluish-green colour: *Copper-rust*, also the so-called *Verdigris*. (Bonsdorff, *Pogg.* 42, 337.) Copper which has been buried for centuries in damp earth, is found to be converted externally into carbonate of the protoxide (*Aerugo nobilis*), and internally into crystalline dioxide. Green carbonate of the protoxide soon shows on the outside, dioxide beneath that, and unaltered metal in most of all. (Nöggerath, *Schw.* 43, 129.) According to Becquerel (*Ann. Chim. Phys.* 51, 106), green and blue carbonate soon forms on the outside, while the inner portion is almost wholly converted into cubes and cubo-octohedrons of the dioxide.—In a dilute solution of caustic potash, in which iron remains bright, copper becomes oxidized, and with peculiar rapidity at those parts where it is in contact with air and water at the same time. (Payen, *J. Chim. Méd.* 9, 205.) Copper wetted with strong potash- or soda-ley, acquires a brown-black colour by exposure to the air for a few hours—more slowly when moistened with a dilute solution; still more slowly when it is immersed in a dilute alkaline solution placed in an open vessel, but even then more quickly than in pure water. In water containing $\frac{1}{300}$ part of caustic potash, the blackening takes place in a few days; in a very dilute solution of potash, the alteration produced is but slight; and in lime-water, even when diluted with twice its own volume of water, the copper retains its lustre. (A. Vogel, *J. pr. Chem.* 14, 107.)—Copper oxidizes readily in saline solutions; less easily when carbonate of potash is added to the liquid. In a solution of common salt mixed with carbonate of soda, it becomes covered in a few days with a brown film of dioxide, whereby it is bronzed. (Wetzlar, *Schw.* 49, 488).—3. At a white heat, copper slightly decomposes vapour of water, very slowly forming a small quantity of protoxide. (Regnault, *Ann. Chim. Phys.* 62, 364.) It does not liberate hydrogen gas when boiled with hydrochloric acid (A. Vogel, *Schw.* 32, 301), or with dilute sulphuric acid.—4. It decomposes heated oil of vitriol and nitric acid, liberating sulphurous acid in the one case, and nitric oxide in the other, and forming a salt of the protoxide.

A. Cuprous Oxide. Cu^2O.

Di-oxide of Copper, Oxyde Cuivreux, Red Oxide of Copper, Rothes Kupferoxyd, Protoxide de Cuivre.—Found native in the form of *Red Copper-ore*, which appears to have been formed by oxidation of copper in the humid way.

Preparation.—1. By exposing very thick copper wires under the muffle, first for half an hour to a white heat, and then for several hours

to a dull red heat. The cuprous oxide is deposited on the remaining button of metal in black masses of crystals, which yield a purple-red powder. (Marchand, *J. pr. Chem.* 20, 505.)—2. One part of finely-divided metallic copper obtained by precipitation with iron, is mixed with 1¼ pt. cupric oxide, and exposed in a close vessel to a low red heat (Chenevix); or copper plate is arranged in alternate layers with cupric oxide and ignited,—after which the superabundant metal may be easily separated from the red oxide. (Berzelius.)—3. A mixture of 24 parts of dehydrated blue vitriol, and 29 parts of copper filings, is heated in a porcelain retort or a well-closed crucible—whereupon sulphurous acid is evolved—and the vessel is not opened till perfectly cold. The red-brown, granular mass thus obtained, yields a red powder, and is free from sulphur and metallic copper. (Ullgren, *Pogg.* 55, 527.)—4. By heating 100 parts of crystallized blue vitriol with 57 parts of crystallized monocarbonate of soda, till the water of crystallization is expelled—mixing the powdered residue with 25 parts of copper filings—stamping the mixture closely into a crucible—exposing it for 20 minutes to a white heat—and washing the mass, after cooling and pulverization, with water. This process yields about 50 parts of fine-coloured red oxide. If twice the quantity of carbonate of soda is used, sufficient, that is to say, to take up all the sulphuric acid, the dioxide obtained is mixed with protoxide. (Malaguti, *Ann. Chim. Phys.* 54, 216; also *J. pr. Chem.* 2, 167.)—5. A mixture of 5 pts. dichloride of copper (prepared by evaporating a solution of the protochloride, and fusing the residue in a crucible) and 3 pts. anhydrous carbonate of soda, is fused at a gentle heat in a covered crucible, and the residue exhausted with water. (Wöhler & Liebig, *Pogg.* 21, 581.)—6. Dichloride of copper is decomposed with aqueous carbonate of potash in a closed retort; the precipitated cuprous hydrate washed in the retort with well-boiled water, the air being carefully excluded; and then heated in the retort. (Proust.)—7. Hydrated protoxide of copper is heated in a solution of sugar containing potash. The hydrate gradually dissolves, and immediately falls down again in the form of [hydrated?] yellow dioxide, being reduced to that state by the sugar. (Hunton, *Phil. Mag. J.* 11, 154.)—Or, more conveniently: An aqueous solution of 1 pt. blue vitriol and 1 pt. sugar is heated with a sufficient quantity of soda to redissolve the precipitated cupric hydrate, and the blue liquid gently warmed. The cuprous oxide is then precipitated, free from water, in the form of a powder which presents a crystalline appearance when examined by the microscope. (Mitscherlich, *J. pr. Chem.* 19, 450.)—Or a cold saturated solution of blue vitriol is poured into potash-ley; 9 parts of the resulting hydrate—after being washed upon linen, and pressed to free it from the greater part of the liquid—diffused by agitation, while yet moist, through a solution of 27 pts. sugar and 60 pts. water; a solution of 18 pts. potash-hydrate in 60 pts. water is then added to the liquid; the whole agitated and filtered through linen; and the dark blue liquid heated, with constant stirring, in the water-bath,—whereupon it is decomposed and yields a deposit of fine-coloured, red cuprous oxide. The product is washed with water, pressed between paper, and carefully dried. (Böttger, *Ann. Pharm.* 39, 176.)

Properties.—Cuprous oxide, both natural and artificial, crystallizes in forms belonging to the regular system. *Figs.* 1, 2, 3, 4, 5, 6, 8, and others; cleavage parallel to *o*. Phillips (*Ann. Phil.* 17, 150), by strongly igniting artificial cuprous oxide in a crucible, obtained alternate layers of copper and cuprous oxide, the latter crystallized in cubes and octohedrons.

Harder than calcspar. Sp. gr. of the native oxide 5·3 (P. Boullay); of very pure crystals 5·749 at 4° in vacuo (Royer & Dumas); 5·751 (Karsten); 6·093 (Herapath). Lustre adamantine, inclining to semi-metallic; colour brownish cochineal-red. The powder, whether of the natural or artificial crystals, has a carmine colour, which is brighter as the oxide is purer.

Copper-bloom, which likewise consists of cuprous oxide, and is classed among red copper-ores, is found in carmine-coloured, capillary crystals, which, according to G. Suckow (*Pogg.* 34, 528), are six-sided prisms perpendicularly truncated, with cleavage parallel to the faces of a rhombohedron, and the angles at the terminal edges=99° 15′. Karsten (*Schw.* 47, 204) found in the ore from Rheinbreitenbach a small quantity of selenium; but according to Suckow, the purer crystals are cuprous oxide, only those which are tarnished containing 1 per cent. of selenium and arsenic.

			Berzelius.	Chenevix.	Proust.
2Cu	64	88·89	88·89 to 88·97	88·5	86·2 to 85·5
O	8	11·11	11·11 „ 11·03	11·5	13·8 „ 14·5
Cu^2O	72	100·00	100·00 „ 100·00	100·0	100·0 „ 100·0

($Cu^2O = 2 \,.\, 395·7 + 100 = 891·4$. Berzelius.)

Decompositions. Reduced to the metallic state by gentle ignition with charcoal or hydrogen gas; also by potassium, somewhat above the melting point of the latter, and with evolution of light and heat. By the action of aqueous sulphuric or phosphoric acid, or of cold, very dilute nitric acid, it is resolved into metallic copper, which separates in the form of a red powder, and cupric oxide, which dissolves. Bromine-water converts it into bromide of copper and cupric oxide. (Balard.)—The statement of Proust, that cuprous oxide is converted by a strong heat into a brown mixture of cupric oxide and metallic copper, is inconsistent with the above-described methods of preparing the oxide (1, 3, 4, and 5).

Combinations.—a. With Water.—Hydrated Cuprous Oxide, or Cuprous Hydrate.—1. By decomposing the dichloride of copper, or the solution of that compound in hydrochloric acid, with excess of potash or soda. (Proust.)—By heating recently precipitated cupric hydrate with an aqueous solution of milk-sugar containing a little carbonate of soda, to the boiling point for a few minutes, till it assumes an orange-yellow colour, then diluting with water and washing. (Böttger.)—Orange-yellow powder.—The hydrate prepared by (1) when heated for some time to 100°, retains its water and its colour, becoming, however, somewhat darker; at 360° it gives off its water, which amounts to only 3 per cent. and still retains its orange-yellow colour, which does not change to red till the heat is increased to whiteness. (Mitscherlich, *J. pr. Chem.* 19, 450.)—By exposure to the air, it is converted into hydrated cupric oxide.

b. With a few acids, forming the Salts of Cuprous Oxide or Cuprous Salts.—*Subsalts of Copper.*—Since cuprous oxide is decomposed by most acids, *e. g.* phosphoric, sulphuric, oxalic, tartaric, acetic, and very dilute nitric acid, yielding metallic copper and cupric oxide, which dissolves, and is moreover oxidized by certain other acids, it follows that very few cuprous salts are known. ¶ According to Fremy (*N. Ann. Chim. Phys.* 23, 391), hydrated cuprous oxide, as obtained by decomposing the solution of the dichloride in hydrochloric acid with

carbonate of potash or soda, dissolves in all acids, even the weakest, producing *cuprous* salts; but when it becomes anhydrous—a change which may take place even when it is immersed in water, and under circumstances not yet understood, it loses this basic property, and is decomposed by acids. ¶ Cuprous salts are either colourless or red; they are converted into cupric salts by exposure to the air in the moist state, also by nitric or hypochlorous acid. With hydrosulphuric acid or hydrosulphate of ammonia, they give a black precipitate of disulphide of copper insoluble in excess of the re-agent. Fixed alkalis separate orange-yellow cuprous hydrate. Ammonia and carbonate of ammonia in excess, form a colourless mixture, which turns blue on exposure to the air. Carbonate of potash throws down the orange-yellow hydrate; iodide of potassium: brownish-white diniodide of copper; ferrocyanide of potassium: a white precipitate which become brown-red by exposure; and ferricyanide of potassium, a brown-red precipitate.

c. With Ammonia.—*d.* With borax and glass-fluxes, forming red compounds.

B. Cupric Oxide. CuO.

Protoxide of Copper, Oxyde Cuivrique, Black Oxide of Copper, Schwarzes Kupferoxyd, Deutoxyde de Cuivre.—Found native in the form of *Black Copper* (*Kupferschwärze*).

Preparation.—1. By prolonged ignition of copper in the air.—2. By raising the sulphate of cupric oxide to an intense red heat, or the carbonate or nitrate to a moderate red heat.—3. According to Ficinus, this oxide may be conveniently prepared by exposing a mixture of 1 pt. copper filings, and 2 pts. deliquesced cupric nitrate to the air, till the whole is converted into a basic salt, and then igniting that salt.

Properties.—Cupric oxide may be obtained in the crystalline state by heating half a gramme of it with 2 or 3 grammes of potash-hydrate to commencing redness, washing the mass when cold with water, and separating the flocculent cupric oxide from the crystalline portion by levigation.—The crystallized oxide consists of regular tetrahedrons having a strong lustre. (Becquerel, *Ann. Chim. Phys.* 51, 122.)—Cupric oxide commonly takes the form of brown-black, brittle scales and granules, or of a brown-black powder, which, when strongly heated, assumes for a while a pure black tint. Specific gravity 6·401 (Herapath), 6·4304 (Karsten). Fuses at a very high temperature, and solidifies in a mass having a crystalline fracture.

		Proust.	Berzelius. *earlier.*	Berzelius. *later.*	Gay-Lussac.
Cu	32	80	80 to 80·13	79·825	80·28
O	8	20	20 „ 19·87	20·175	19·72
CuO	40	100	100 „ 100·00	100·000	100·00

(CuO = 395·7 + 100 = 495·7. Berzelius.)

Decompositions.—Reduced to the metallic state by gentle ignition with hydrogen gas or charcoal. It is very easily reduced on charcoal before the blowpipe. If its powder be heated in a spoon to a temperature short of redness, and then introduced into a vessel filled with hydrogen gas, it is reduced to the metallic state, with incandescence and formation of water. (Berzelius.) The lowest temperature at which cupric

oxide can be reduced by hydrogen is the boiling point of linseed oil. (Schrötter.) Cupric oxide is likewise reduced to the metallic state by potassium and sodium, at temperatures somewhat below the melting points of those metals, and with vivid incandescence. With fused cyanide of potassium it yields copper and cyanate of potash. (Liebig.)—When gently ignited with metallic copper, it is converted into cuprous oxide.—With phosphorus at a red heat, it yields phosphide of copper and phosphate of cupric oxide.—Mixed with phosphoric oxide, it detonates slightly on the approach of a red-hot coal, and is converted into phosphate of cupric oxide and brightly-glowing fused globules of phosphide of copper. (Leverrier.)—A mixture of cupric oxide with excess of sulphur is resolved at a red heat into sulphide of copper, sulphurous acid, and a trace of cupric sulphate :

$$2CuO + 2S = Cu^2S + SO^2.$$

If, on the contrary, the cupric oxide is in excess, cuprous oxide and cupric sulphate are produced, and only a trace of sulphurous acid, excepting when the heat is raised to the point at which the cupric sulphate is decomposed. (Max Jordan, *J. pr. Chem.* 28, 222.)

$$7CuO + S = CuO, SO^3 + 3Cu^2O.$$

When protoxide of copper is boiled with aqueous protochloride of tin, bioxide of tin is precipitated, and dichloride of copper dissolved. (Proust; A. Vogel, *Kastn. Arch.* 23, 85.)—Hydrated protoxide of iron and hydrated protoxide of copper, are converted by mutual decomposition into hydrated sesquioxide of iron and hydrated dioxide of copper, the latter of which may be dissolved out by ammonia. (Levol, *Ann. Chim. Phys.* 60, 320; also *J. pr. Chem.* 14, 115.)

$$2FeO + 2CuO = Fe^2O^3 + Cu^2O.$$

In presence of potash or soda, and with the aid of heat, cupric oxide is decomposed by arsenious acid, the products being cuprous oxide and arseniate of potash. The decomposition is effected by mixing 160 pts. (4 At.) of cupric oxide with 100 pts. (rather more than 1 At.) of arsenious acid, and with excess of soda, and digesting the mixture at a gentle heat, with frequent agitation, till all the protoxide of copper is converted into dioxide : the solution contains arseniate of soda :

$$4CuO + AsO^3 = 2Cu^2O + AsO^5.$$

When ammonia is used in place of soda, only half of the protoxide of copper is converted into dioxide ; the rest remains dissolved in the ammonia, forming a blue solution, and no decolorization takes place till potash or soda is added. A mixture of arsenious acid with carbonate of potash or soda or quick-lime, does not convert the protoxide of copper into the dioxide. (Bonnet, *Pogg.* 37, 300.)—When protosulphide of iron is fused with protoxide of copper, sulphide of copper is formed. (Karsten, *Schw.* 66, 401.)—Protoxide of copper is reduced to the state of dioxide by boiling it with various organic substances, *e. g.* with oil of turpentine.

Combinations.—a. With Water. — Hydrated Cupric Oxide, or Cupric Hydrate.—Formed by precipitating a dissolved cupric salt in the cold, with a slight excess of dilute caustic potash, quickly washing the blue precipitate with cold water, and drying it at the ordinary temperature of the air. The hydrate generally turns black from admixture of anhydrous

cupric oxide, even during the washing and drying. According to Palmstedt, it is more durable when obtained by the action of caustic potash on carbonate of cupric oxide previously well washed with water.—After drying, it forms greenish-blue, friable lumps, having a conchoidal fracture; its taste is strongly metallic.—In the dry state it remains undecomposed, even at 100°, but at a somewhat higher temperature, it is converted into anhydrous black oxide; thus, if the hydrate be heated on paper, the change takes place at a temperature not high enough to char the paper. Under water it likewise sustains a temperature of 100° [†] without alteration, but if kept for some time under that liquid, it is converted in the black oxide, with considerable diminution of volume. It is also converted into black oxide by boiling in solution of caustic potash. Alcohol does not decompose the hydrate either in the fresh or in the dry state. (Proust, *Ann. Chim. Phys.* 32, 41.)—Much of the *Blue verditer* or *Bremen green* which is found in commerce, consists of hydrated cupric oxide. A solution of blue vitriol is precipitated by caustic potash of 15° B, the precipitate washed, then again treated with caustic potash of 15°....18° B, and lastly well washed. The potash-solution must contain a little carbonic acid—in the state, in short, in which it is obtained by slaking 50 parts of lime in an aqueous solution of 80 parts of pearl-ash; otherwise the colour will be spoiled. (Gentle.)

					Proust.
CuO	40	....	81·63	.....	75
HO	9	....	18·37	.....	24
CO^2		....		.....	1
CuO, HO	49	....	100·00	.....	100

¶ According to Fremy (*N. Ann. Chim. Phys.* 23, 161), hydrated cupric oxide obtained by precipitating a solution of blue vitriol in the cold with a large excess of potash, and then drying in vacuo, contains CuO + 2HO. ¶

b. With Acids, forming the Salts of Cupric Oxide, or Cupric Salts.—*Protosalts of Copper.*—Cupric oxide has a stronger affinity for acids than cuprous oxide, dissolving in them easily, and with evolution of heat, even after ignition; the hydrate and carbonate dissolve with still greater facility. The last-mentioned compounds likewise dissolve in ammoniacal salts, and liberate the ammonia on boiling. The anhydrous cupric salts are mostly white, the hydrated salts have a blue or green colour. They are for the most part soluble in water, and the solutions have a metallic taste, and redden litmus. At a red heat, they give off their acid, provided the acid is volatile; the sulphate, however, requires a strong heat to decompose it. With carbonate of soda on charcoal in the inner blowpipe-flame, they yield metallic copper. With borax and microcosmic salt, they behave like cupric oxide. When fused on the platinum wire with microcosmic salt or common salt, they impart a blue colour to the blowpipe-flame.

Copper is precipitated in the metallic state from solutions of cupric salts: 1. By *Phosphorus.* In this manner it may be precipitated from the sulphate. (Boeck, *Diss. de reductione metallorum.* Tubingen, 1804. Grotthuss.) In a close vessel, the solution becomes decolorized in a few days, no longer containing copper, but only sulphuric and phosphoric acid, and the phosphorus is found to be covered with a shining coating of copper; after some months, a black deposit of phosphide of copper is found between this film and the remaining phosphorus. (A. Vogel,

J. pr. Chem. 8, 109.)—To reduce copper in any considerable quantity from the nitrate by phosphorus, the solution used must be dilute; in a concentrated solution, a black crust is formed on the phosphorus with but little metallic copper; and if the air has access to the liquid for some time, the whole deposit vanishes, with formation of bluish-white flakes of cupric phosphate. (Boeck.) In close vessels, the action of phosphorus on cupric nitrate is the same as on the sulphate, very bright metallic copper being deposited, and so large a quantity of phosphide that the remaining phosphorus is blackened by it throughout its whole substance; after standing for some time, the copper becomes less bright, inasmuch as the nitric acid set free in the liquid acts upon it and evolves nitric oxide. (A. Vogel.) A dilute solution of cupric acetate kept in contact with phosphorus in a closed vessel, becomes paler, deposits greenish-white flakes of cupric phosphate, and covers the phosphorus, first with a black and then with a copper-coloured deposit. (A. Vogel.)—Phosphorus immersed in a solution of protochloride of copper becomes covered with a black deposit, a large quantity of white and reddish-white dichloride of copper being likewise precipitated. (Boeck.)—In a dilute solution of protochloride of copper, phosphorus becomes covered with metallic copper; but in a concentrated solution, it first produces an abundant precipitation of white dichloride of copper, and then becomes blackened throughout its substance by phosphide of copper. The liquid thereby acquires at first a dark and afterwards a pale yellow colour, and contains dichloride of copper dissolved in hydrochloric acid; when concentrated by boiling, it deposits this compound and gives off hydrochloric acid; and on further concentration, it evolves phosphuretted hydrogen gas, and yields a black precipitate of phosphide of copper. (A. Vogel.) Hence it appears to contain phosphorous acid.

2. By *Hypophosphorous acid.*—A solution of blue vitriol gently heated with this acid, gives off hydrogen gas and deposits copper.

3. By *Zinc, Cadmium, Tin, Lead, Iron, Cobalt, Nickel,* and *Bismuth.*—Nitrate of cupric oxide is most quickly decomposed by zinc; then follows lead, then tin, and then cadmium. (Fischer, *Pogg.* 8, 492.)—*Zinc* throws down from cupric salts, even when they contain a large excess of acid, first black copper containing zinc, and afterwards pure copper having its characteristic red colour; because the precipitate, as it increases, falls off from the zinc, and forms a galvanic circuit for itself, in consequence of which the zinc which it contains is dissolved. (Wetzlar, *Schw.* 50, 98.)—From protochloride of copper, zinc precipitates metallic copper and likewise the dichloride. (Fischer.)—Cupric nitrate dissolved in alcohol is likewise reduced by zinc. (Fischer. *Gilb.* 72, 289.)—Zinc immersed in a solution of 1 pt. blue vitriol in 3 pts. water at 90°, throws off a large quantity of hydrogen gas, and precipitates cupric oxide as well as copper. (Leykauf, *J. pr. Chem.* 19, 124.)—*Cadmium* throws down from the nitrate, black copper containing cadmium, and from the chloride, a mixture of copper and the dichloride. (Fischer.)—*Tin* throws down copper from the sulphate, chloride, and nitrate, but not from the neutral acetate. When a solution of blue vitriol not containing any free acid, is enclosed in a bottle together with tin-foil, it changes after a while into a colourless solution of stannous sulphate, which is not rendered permanently turbid by the addition of small quantities of potash, and therefore appears to contain free acid; and on the surface of the tin there is deposited an alloy of tin and copper, partly black and partly brass-yellow, a few laminæ of the same substance being likewise attached to the sides of the vessel.

(Wetzlar, *Schw.* 50, 99.) When tin is immersed in a solution of cupric nitrate, stannic oxide is precipitated together with the tin. (Fischer.)—*Lead* precipitates copper from the chloride or nitrate but not from the sulphate. (Wetzlar.) According to Fischer, however, a slight precipitation takes place even in the sulphate. Copper reduced by lead exhibits the metallic lustre. (Fischer.)—*Iron* has no action on a solution of cupric nitrate made as nearly neutral as possible, or, at the utmost, a very slight action after long exposure to the air; acidulated copper solutions are rapidly precipitated by iron. (Fischer, *Pogg.* 8, 492.) If the solution of cupric nitrate be mixed with the smallest quantity of silver-nitrate, the iron is thereby rendered passive (I. 358–361), and does not precipitate the smallest quantity of copper. (Wetzlar, Fischer, *Pogg.* 10, 604.) From a solution of blue vitriol, iron precipitates the copper rapidly, first in the form of a deposit having the characteristic red colour of copper, and afterwards as a dark brown, pulverulent mixture of copper and basic sulphate of ferric oxide. (Fischer.) Copper precipitated from a neutral solution of the sulphate is black from admixture of iron, but turns red and gives off hydrogen when immersed in dilute sulphuric acid. The precipitated copper may be mixed with iron, even when the solution contains free acid. (Wetzlar.) From protochloride of copper, iron precipitates the dichloride as well as metallic copper. (Fischer.) Copper is likewise reduced by iron from the alcoholic solution of the protochloride. A solution of blue vitriol containing 1 part of copper in 25,000 reddens iron after the lapse of two hours; when the quantity of liquid equals from 500,000 to 1,000,000 parts to 1 part of copper, scarcely any visible effect is produced. (Lassaigne, *J. Chim. Méd.* 8, 580.) The limit at which the iron ceases to be reddened, shows itself in a solution containing 1 pt. of copper in 156,000, the liquid being acidulated with a drop of nitric acid. (Harting, *J. pr. Chem.* 22, 51.) Iron does not precipitate an alcoholic solution of cupric nitrate, even on the addition of nitric acid; neither is an aqueous solution of tartrate of cupric oxide and potash precipitated by iron. (Wetzlar.)—*Nickel* produces no precipitate in a copper-salt already formed; but when an alloy of nickel and copper is acted upon by a quantity of nitric acid not sufficient to dissolve it all, the undissolved portion is found to be coated with copper. (Fischer, *Pogg.* 12, 504.) Bismuth precipitates cupric nitrate only at a boiling heat, and even then but imperfectly; from the protochloride, it throws down dichloride of copper mixed with oxychloride of bismuth. (Fischer.)—Copper-salts are not reduced by brass or by the alloys of silver with zinc, tin, and lead. (Fischer, *Pogg.* 12, 504.)

4. By *Organic Compounds.*—*Sugar* boiled with a solution of blue vitriol throws down metallic copper. (A. Vogel.)—*Wood* produces the same effect after long contact. (Clement, Bischof, *vid.* p. 400.)—The aqueous solution of cupric oxide in cream of tartar, when diluted with a large quantity of water and gently heated, deposits copper in the form of a soft red powder. From a copper solution kept for some days in a glazed pot which had been used for cooking, a net of copper was deposited, corresponding in form to the cracks in the glazing. (Taillefer, *Ann. Chim. Phys.* 31, 100.)

Sulphurous acid, even with the aid of heat, does not exert any reducing action on the solutions of cupric oxide in the stronger acids; but alkaline sulphites colour them green by formation of cupric sulphite, which is then resolved, slowly at ordinary temperatures, but immediately on boiling, *into soluble* cupric sulphate and precipitated cuprous sulphite. If the

alkaline sulphite is in excess, nearly all the copper is precipitated. (Berthier, *N. Ann. Chim. Phys.* 7, 80.) Sulphite of ammonia forms a bulky light brown precipitate with cupric salts. (H. Rose.) A solution of cupric sulphate heated with sulphurous acid, and likewise a solution of cupric phosphate or arseniate in sulphurous acid forms with a small quantity of potash a yellow precipitate [of sulphite of cuprous oxide and potash ?]. (A. Vogel, *J. pr. Chem.* 30, 39.) If the cupric oxide is united with one of the weaker acids, as with acetic or formic acid, a precipitate of cuprous oxide [sulphate] is formed on heating the liquid. (A. Vogel.)—Aqueous protochloride of tin throws down from cupric salts a white crystalline powder consisting of dichloride of copper.—Sugar likewise reduces cuprous oxide from many cupric salts. Sugar boiled with an aqueous solution of cupric acetate precipitates dioxide of copper, and when boiled with the protochloride, it throw down the dichloride. (A. Vogel.)

Phosphuretted hydrogen gas passed through a solution of blue vitriol, slowly throws down triphosphide of copper.—Hydrosulphuric acid and alkaline hydrosulphates throw down from cupric salts a precipitate of protosulphide of copper, insoluble in excess of the reagent. If the solution is very dilute, merely a brownish colouring is produced, and this effect is visible even when the proportion of cupric oxide is only 1 pt. in 100,000 of the liquid (Pfaff), or 1 pt. metallic copper in 200,000 pts. of the liquid. (Lassaigne.) A solution of 1 pt. crystallized cupric acetate in 10,000 water and 2,500 hydrochloric acid still shows a distinct colouring with sulphuretted hydrogen; with 1 pt. cupric oxide in 15,000 water and 7,500 hydrochloric acid, a slight colour: but with 1 pt. cupric oxide in 40,000 water and 20,000 hydrochloric acid, the effect is no longer visible. (Reinsch, *J. pr. Chem.* 13, 133.) Paper soaked in a solution of copper and then perfectly dried, does not blacken in dry sulphuretted hydrogen gas, and absolute alcohol which has absorbed 6 volumes of sulphuretted hydrogen, has no action on anhydrous copper salts. (Parnell, *J. pr. Chem.* 26, 190.)—The hydrated sulphides of manganese, cobalt, and nickel throw down sulphide of copper from a solution of the sulphate. (Anthon.) A copper solution boiled with an alkaline hyposulphite deposits black sulphide of copper, with formation of sulphuric acid. (H. Rose, *Pogg.* 33, 241.) Probably in this manner:

$$CuO,SO^3 + KO,S^2O^2 = CuS + KO,2SO^3.$$

A solution of blue vitriol is immediately decolorized by hyposulphite of soda, and then, on the addition of hydrochloric acid, deposits all the copper in the form of rust-brown sulphide, probably CuS^2; the precipitate turns black if kept for some time under the liquid, and shows no tendency to oxidate by exposure to the air. (Himly, *Ann. Pharm.* 43, 151.)—Iodide of potassium added to a cupric salt throws down white diniodide of copper, the liquid turning brown from separation of iodine: the precipitate dissolves in excess of iodide of potassium.

Potash or soda added to a cupric salt, in quantity not sufficient to decompose it completely, throws down at first a blue precipitate of hydrated cupric oxide, which, however, on agitation, takes up a portion of the undecomposed salt, and forms with it a green basic salt. An excess of the alkali throws down the hydrated oxide in bulky blue flakes, which, on boiling the mixture, collect together in the form of a black powder, consisting of the anhydrous oxide. ¶ According to Völker (*Ann. Pharm.* 59, 34), strong caustic potash dissolves a consider-

able quantity of cupric oxide, and the solution may be diluted with a considerable quantity of water without depositing the oxide. ¶ — Ammonia added by degrees, and with constant agitation, to the solution of a cupric salt, first throws down a green basic salt, and afterwards the blue hydrate; an excess of ammonia dissolves the precipitate, forming a deep blue solution. A copper solution diluted so far as to be colourless, still becomes distinctly blue on the addition of ammonia. The blue colour thus produced is still visible in a solution of 1 pt. cupric oxide in 2000 parts of acid and water (Pfaff); with 1 part of copper in 11,750 parts of liquid (Harting); with 1 part of copper in 100,000 parts of liquid (Sarzeau, *J. Pharm.* 16, 516; Lassaigne). The discrepancy of these statements may perhaps arise from the different quantities of liquid used: the greater the mass of liquid, the more readily will the blue colour be seen.—Potash added to a solution containing a cupric and a ferrous salt in equal number of atoms, throws down a mixture of cupric and ferrous hydrates. Ammonia added in excess yields a precipitate of ferric hydrate and a colourless solution of cuprous oxide in ammonia; a smaller quantity of ammonia throws down a purple-red mixture of ferric hydrate and cuprous oxide. (Levol, *Ann. Chim. Phys.* 65, 320.)—Carbonate of potash or soda throws down—with evolution of carbonic acid—a greenish-blue precipitate of cupric carbonate, a small quantity of which dissolves in excess of the alkaline carbonate, forming a bluish solution. On boiling the mixture, the precipitate is converted into black oxide of copper, the change being more complete as the excess of the alkaline-carbonate is greater; if the copper-salt is in excess, the precipitate remains green, and consists of a basic salt not containing carbonic acid.—Carbonate of ammonia produces the same precipitate, but, when added in excess, dissolves it abundantly, forming a deep blue solution.—The carbonates of baryta, strontia, and lime, and likewise carbonate of magnesia, do not precipitate cupric salts in the cold, but completely at 60°. (Demarçay, *Ann. Pharm.* 11, 240.)—Phosphate of soda throws down greenish-white cupric phosphate, and chromate of potash produces a red-brown precipitate of cupric chromate.

Oxalic acid throws down from cupric salts a pulverulent bluish-green-white precipitate of cupric oxalate; and monoxalate of potash in excess precipitates blue oxalate of cupric oxide and potash. Even dilute solutions containing excess of acid, are precipitated by oxalic acid. (Wackenroder.)—Cyanide of potassium precipitates yellowish-green protocyanide of copper, which, on heating the liquid, first turns yellow and then white, and dissolves in excess of the cyanide of potassium.—Ferrocyanide of potassium yields, with concentrated cupric solutions, a dark brown-red magma, and with dilute solutions, a deep purple precipitate; to very dilute solutions, it imparts a reddish colour. The reddish colour is still visible in a solution of 1 part of cupric oxide in 78,000 parts of liquid (Harting); with 1 pt. cupric oxide in 200,000 of liquid (Pfaff); with 1 pt. copper in 400,000 liquid (Lassaigne); with 1 pt. copper in 1,000,000 parts of liquid (Sarzeau).—Ferricyanide of potassium forms, with cupric salts, a thick brownish-yellow precipitate, as little soluble in hydrochloric acid as the preceding.—Xanthonate of potash added to cupric salts, throws down yellow flakes.—Tincture of galls does not precipitate the solutions of cupric oxide in the stronger mineral acids, except on the addition of acetate of potash; in that case, and likewise from a solution of cupric acetate, it throws down a red-brown magma.—Concentrated copper solutions immediately impart to tincture of guiacum a

blue colour, which soon turns green; dilute solutions produce the same effect on the addition of hydrocyanic acid. Tincture of guiacum is prepared by steeping 1 part of guiacum-wood in 4 parts of water; the reaction is still visible in a solution containing 1 part of copper-salt in 450,000 parts of water. (Pagenstecher, *N. Tr.* 3, 1, 404.)

Cupric salts, which are insoluble in water, dissolve in sulphuric, hydrochloric, or nitric acid, or at all events, give up their cupric oxide to the acid.

c. With Alkalis.—*d.* Soluble in oils, sugar, &c.

C. *Peroxide of Copper?*

1. Formed by agitating the hydrated protoxide with a large excess of very dilute peroxide of hydrogen at a temperature of 0°.—2. By mixing nitrate of cupric oxide with excess of aqueous peroxide of hydrogen, and precipitating the copper at 0°, by caustic potash added in moderate excess.—The resulting peroxide of copper is washed with cold water, pressed between bibulous paper, and dried in vacuo.—Yellowish-brown powder (or olive-green, if contaminated with hydrated cupric oxide), tasteless, and without action on vegetable colours. Contains nearly twice as much oxygen as the protoxide. At a temperature short of 100°, it gives off oxygen, and is converted into protoxide; in the moist state, it decomposes in the course of 12 hours, even at ordinary temperatures. The decomposition is greatly accelerated by the presence of strong caustic potash.—Insoluble in water. With acids, it forms ordinary cupric salts and peroxide of hydrogen. (Thénard.) It is perhaps not a higher oxide of copper, as Thénard supposes, but rather a compound of cupric oxide with peroxide of hydrogen.

¶ D. *Cupric Acid?*

Not known in the separate state. Some of its salts have been obtained in the state of solution, by passing chlorine gas into potash- or soda-ley, in which hydrated cupric oxide is diffused; but they cannot be obtained in the solid state, inasmuch as they are decomposed with violent evolution of oxygen soon after their formation. Cuprate of lime has however been obtained in the form of a beautiful rose-coloured substance, by mixing chloride of lime with a solution of nitrate of cupric oxide; it decomposed but slowly. (Krüger, *Pogg.* 72, 445.) According to Crum (*Ann. Pharm.* 55, 213), the oxygen-compound of copper contained in this salt is a sesquioxide. Cu^2O^3. ¶

Copper and Hydrogen.

Hydride of Copper?—A solution of blue vitriol and hypophosphorous acid, heated not above 70°, deposits a yellow precipitate, which soon turns red-brown. It contains 98·78 pts. copper to 1·22 hydrogen ($=Cu^2H$), gives off hydrogen when heated, takes fire in chlorine gas, and when treated with hydrochloric acid, is converted into dichloride of copper, with evolution of a double quantity of hydrogen gas. (Wurtz, *Compt. rend.* 18, 702.)

Copper and Carbon.

A. Carbide of Copper.—Often produced in the toughening of copper, when the metal is fused, according to the English method, under a layer of charcoal powder: *Overpoled Copper* (Vivian, *Ann. Phil.* 21, 121).—Obtained also by arranging copper plate in alternate layers with lamp-black, heating to redness for several hours, and then raising the temperature to the melting point of copper. In this process, the copper takes up at most 0·2 per cent. of carbon. (Karsten, *Schw.* 66, 395.) —Copper containing carbon has a pale yellowish-red colour and strong metallic lustre, and the surface of the mass solidified after fusion exhibits a strinted texture. After fusion, it has a strongly lustrous, yellowish-red, coarsely fibrous, and indented fracture, and after hammering, a yellowish-red sinewy fracture. It is ductile at ordinary temperatures, but at a low red heat, it breaks under the hammer; even 0·05 per cent. of carbon makes it slaty at a red heat. When fused in the air, and especially if stirred, it readily gives up its carbon. (Karsten.)

The orange-yellow precipitate which is produced by adding carbonate of soda to a solution of dichloride of copper in hydrochloric acid, and assumes a brick-red colour when washed with cold water, is merely hydrated cuprous oxide, free from carbonic acid. (Gmelin.)

B. Carbonate of Cupric Oxide, or Cupric Carbonate.—*a. Dicarbonate.*—The anhydrous salt occurs, according to Thomson (*Outlines of Mineralogy*, 1, 601), in the form of *Mysorine*, which contains 60·75 cupric oxide, 16·70 carbonic acid, 19·50 ferric oxide, and 2·10 silica. It does not appear, however, that this compound can be formed artificially. It is stated, indeed, by Colin & Taillefert (*Ann. Chim. Phys.* 12, 62), that the hydrated compound, when heated by itself or boiled with water, is converted into a brown powder, which is the anhydrous carbonate. But according to Gay-Lussac (*Ann. Chim. Phys.* 37, 335), when the salt is boiled with water for several hours, the whole of the carbonic acid is given off, and the residual black powder is pure cupric oxide; it becomes black even when boiled for a short time only; but it then contains carbonic acid.

Hydrated Dicarbonate.—Found in the form of *Malachite.*—Produced when copper is exposed to the joint action of air and water; *Copper-rust*, or the so-called *Verdigris;*—when moist cupric hydrate is exposed to the air, and more quickly when carbonic acid is passed through water in which the hydrate is diffused; the volume of the hydrate is diminished by conversion into carbonate. On precipitating a cupric salt with carbonate of potash or soda, carbonic acid is at first evolved, and a greenish-blue precipitate formed; this, however, is gradually converted during washing, or immediately on boiling, into the green dicarbonate, the change being produced either by loss of carbonic acid, or (according to Colin & Taillefert) merely by loss of water.—The product is a green powder of the colour of verdigris. It acquires a brighter green colour by washing with hot water: *Mineral green.*—The salt when strongly heated by itself, or when boiled for a short time with caustic potash, leaves a black residue of anhydrous oxide; it is insoluble in water, but dissolves in ammoniacal salts, forming a blue solution.

Malachite forms crystals belonging to the oblique prismatic system. *Fig. 81* and 84; $u : u = 103° 42'$; $i : m = 118° 11'$; cleavage parallel to

2. Also when the triphosphide is deprived of half its phosphorus by passing hydrogen gas over it at the strongest heat that the glass can bear. Black powder, or, after strong ignition, light grey mass having the metallic lustre. On charcoal before the blowpipe it emits a phosphorus-flame. Dissolves easily and completely in nitric acid or aqua-regia, with formation of phosphoric acid. Insoluble in hydrochloric acid. (H. Rose, *Pogg.* 6, 209; 24, 228.)

					H. Rose.
6Cu	192·0	85·94	84·42	to	86·61
P	31·4	14·06	15·58	,,	13·39
Cu^6P	223·4	100·00	100·00	,,	100·00

b. Triphosphide.—1. By passing phosphuretted hydrogen gas over heated protochloride of copper. (H. Rose, *Pogg.* 24, 328.) 2. By passing phosphuretted hydrogen through a solution of blue vitriol:

$$3CuO + PH^3 = Cu^3P + 3HO.$$

Either variety of phosphuretted hydrogen may be used. The precipitation begins, after three quarters of an hour, with a black turbidity which soon increases; a certain quantity of phosphoric acid is always formed at the same time. If the black, flocculent precipitate, after being dried in vacuo over oil of vitriol, be gently heated, it gives off a small quantity of moisture, and assumes the red colour of copper. (H. Rose, *Pogg.* 14, 188; 24, 321.) The black flakes, when washed with boiling water out of contact of air, remain for the most part unaltered; but if the air has access to them, the phosphorus becomes oxidized and metallic copper [or red phosphide?] separates out. (Buff, *Pogg.* 22, 353.)

Prepared by (1): black powder, which, when strongly ignited out of contact of air, is converted into a greyish-black, metallic-looking mass, but does not assume the red colour of copper at any temperature. (H. Rose.) By (2): black flakes, which—after gentle heating in vacuo—assume a copper-red colour, like that of metallic copper precipitated by zinc. (H. Rose.) It does not fuse even at the melting point of glass, but is more fusible than copper. (Landgrebe.)

Phosphide of copper prepared by (1) exhibits a phosphorus-flame on charcoal before the blowpipe; (2) does not. (1) gives off half its phosphorus when very strongly ignited in a current of hydrogen gas. (H. Rose, *Pogg.* 4, 110.) Both varieties dissolve readily in nitric acid, with formation of phosphoric acid, especially that obtained by (2) and not previously heated. Hot oil of vitriol dissolves (2) with evolution of sulphurous acid gas. In hydrochloric acid in an open vessel (2) dissolves more readily than pure copper. (H. Rose.) The phosphide prepared by (2) and not heated, dissolves completely in strong hydrochloric acid, with evolution of non-spontaneously inflammable phosphuretted hydrogen. (Buff.) The preparation (2), when it has not been heated, is permanent in dry air, but when exposed to a moist atmosphere, is converted into phosphate of cupric oxide. Before the blowpipe, it burns to a black bead of cupric phosphate, which on cooling solidifies into a white enamel. (Landgrebe, *Schw.* 53, 464.)

			H. Rose (1).		H. Rose (2).		
3Cu	96·0	75·35	75·34	75·76	to	79·84	
P	31·0	24·65	24·66	24·24	,,	20·16	
Cu^3P	127·4	100·00	100·00	100·00	,,	100·00	

As a small quantity of phosphoric acid is formed in process (2), the analysis of the resulting compound gave rather too little phosphorus. (H. Rose.)

c. *Diphosphide.*—When hydrogen gas is passed over diphosphate of cupric oxide—as obtained by precipitating blue vitriol with diphosphate of soda—at the strongest red heat that the glass tube will sustain, the copper-salt first turns yellow from formation of dioxide, and is subsequently converted—with formation of water—into greyish-black phosphide of copper, which becomes crystalline on cooling. (H. Rose, *Pogg.* 24, 331.)

					H. Rose.
2Cu	64·0	....	67·09	.....	65·09
P	31·4	....	32·91	.....	34·91
Cu^2P	95·4	....	100·00	.....	100·00

Phosphide of copper, containing copper and phosphorus in variable proportions, may be obtained by the following methods : 1. When copper filings are ignited with phosphorus in a retort, 3 parts of copper retain 1 pt. of phosphorus [therefore Cu^3P]. (Marggraf.) The same compound may be formed by throwing phosphorus on red-hot copper filings. (Pelletier.)—2. By igniting 1 part of copper filings under charcoal with 1 part of glacial phosphoric acid not free from lime, and $\frac{1}{8}$ of charcoal powder. (Pelletier, *Ann. Chim.* 1, 103; Saye, *Crell. Ann.* 1792, 1, 33; *A. Gehl.* 3, 704.)—3. By igniting cupric phosphate mixed with charcoal, or contained in a crucible lined with charcoal.—4. By exposing a mixture of 6 or 8 pts. copper, or cupric oxide, 10 bone-ash, 5 pounded quartz, 5 borax, and 1 charcoal, in a crucible lined with charcoal, to the heat of a blast-furnace for an hour. (Berthier.)

The fused phosphide of copper thus obtained is of a pale copper-colour when it contains but little phosphorus, and steel-grey when it contains a larger proportion of that substance. The surface of the fused mass is sometimes covered with four-sided prisms, formed by the junction of octohedrons. (Saye.) It exhibits a laminar texture. (Berthier.) Sp. gr.=7·122. (Saye.) It is as hard as steel, brittle, and has a fine-grained fracture, but is difficult to pulverize. Fuses much more easily than copper. Many varieties of phosphide of copper retain their lustre when exposed to the air; others turn black, and fall to pieces, being converted into phosphate of cupric oxide. Phosphide of copper burns in the air with a phosphorus flame, and is converted into a black slag.

B. Hypophosphite of Cupric Oxide, or Cupric Hypophosphite.—The blue solution of hydrated cupric oxide in cold hypophosphorous acid may be kept unaltered for a long time, and, if very dilute, may be heated without decomposition. On evaporating it, however, even in vacuo at a low temperature, complete reduction of the copper takes place as soon as the liquid reaches a high degree of concentration. (H. Rose, *Pogg.* 12, 291.)

C. Phosphite of Cupric Oxide, or Cupric Phosphite.—By precipitating protochloride of copper with phosphate of ammonia, a beautiful blue precipitate is formed, which may be washed with water and dried at a gentle heat without decomposing. When heated in a retort, it yields a large quantity of water, afterwards gives off abundance of pu· hydrogen gas, turns brown from reduction of copper, and fuses into mixture of metallic copper and cupric phosphate, one portion of whi

as it contains excess of acid, may be dissolved out by water, and the rest by hydrochloric acid. The oxygen of the water, as well as that of the oxide of copper, contributes to the formation of phosphoric acid. The solution of cupric phosphite in aqueous phosphorous acid deposits part of the copper in the metallic state on boiling. (H. Rose, *Pogg.* 12, 292.)

D. Phosphate of Cupric Oxide, or Cupric Phosphate.—*a. Sesbasic.*—An emerald-green ore of copper from Hirschberg on the Saale, having a scaly fracture and concentrically fibrous structure. (Kühn, *Ann. Pharm.* 24, 218.)

$$= 3CuO,PO^5 + 3CuO,HO.$$

			Kühn.
6CuO	240·0	70·92	71·73
PO^5	71·4	21·10	19·21
3HO	27·0	7·98	7·40
$6CuO,PO^5 + 3Aq.$	338·4	100·00	98·34

b. Quintobasic.—Phosphorochalcite, or *Pseudo-malachite.*—Crystalline system the oblique prismatic. *Fig.* 91 and 99, together with *m*-, *f*-, and *z*- faces; $u : u' = 38° 56'$; $i : u = 112° 37'$. Likewise found in fibrous and earthy masses. Sp. gr. 4·2. Harder than fluorspar. Emerald and verdigris-green; yields a pale green powder. When suddenly heated before the blowpipe, it falls to powder; but if slowly heated, it turns black, and fuses on the charcoal to a black bead containing a small granule of copper. The bead, strongly heated with an equal volume of lead, yields copper and fused phosphate of lead-oxide, which crystallizes on cooling. Heated with a small quantity of carbonate of soda, it swells up and then fuses; with a larger quantity, it forms a tumefied, infusible mass; when a still larger quantity of carbonate of soda is used, the saline mass sinks into the charcoal, and leaves copper behind. (Berzelius.) When moistened with hydrochloric acid, it imparts a blue colour to the blowpipe-flame. Easibly soluble in nitric acid and in ammonia.

	Phosphorochalcite.		Lunn. Virneberg.	Arfvedson. Virneberg.	Bergmann. Virneberg.	Bergmann. Ehl.
5CuO	200·0	67·02	62·85	68·20	66·94	65·99
PO^5	71·4	23·93	21·69	24·70	24·20	24·93
3HO	27·0	9·05	15·45	5·97	7·89	9·06
$5CuO,PO^5 + 3Aq.$	298·4	100·00	99·99	98·87	99·03	99·98

According to Lunn's analysis, it is $5CuO,PO^5 + 5Aq.$; according to Kühn (*Ann. Pharm.* 51, 123), it is $3(CuO,PO^5) + 3(CuO,HO)$.

¶ *Cupric Phosphate* from *Liebethin.*—Fibrous, separating in concentric scales; with a waxy lustre on the fractured surface, and a satiny lustre on the outer surface; looks as if it had been fused. When heated to redness, it splits asunder with violence, but without noise; even in the state of fine powder, it is forcibly scattered about when ignited.

			Kühn.
5CuO	200·0	69·13	69·61
PO^5	71·4	24·64	24·13
2HO	18·0	6·23	6·26
$3(CuO,PO^5) + (2CuO,HO)$	289·4	100·00	100·00 ¶

c. Quadrobasic.—Liebethenite.—Crystalline system the right prismatic. *Fig.* 54. $u : u' = 84° 58'$; $i : i' = 111° 58'$. Sp. gr. 3·6 to 3·8. Harder than calcspar. Colour olive-green inclining to blackish-green; translucent, with a waxy lustre. Exhibits the same chemical relations as phosphorochalcite.

	Liebethenite.		Berthier (*crystallized*).
4CuO	160·0	64·15	63·9
PO^5	71·4	28·63	28·7
2HO	18·0	7·22	7·4
$4CuO,PO^5+2Aq.$	249·4	100·00	100·0

According to Kühn, it is $3CuO,PO^5+3CuO,HO$.

d. Terbasic.—Precipitated on mixing a cupric salt with diphosphate of ammonia, potash, or soda [in excess?], the liquid becoming acid. (Mitscherlich.)—Bluish-green powder, which when heated gives off water and turns brown. When ignited with charcoal, it yields phosphide of copper. Insoluble in water, but dissolves easily in acids, even in phosphoric, acetic, and sulphurous acid, the latter not causing the formation of cuprous oxide; slightly soluble in ammoniacal salts.

e. Bibasic.—Precipitated from copper-salts by diphosphate of soda [added in insufficient quantity?]. When heated to redness in hydrogen gas, it turns yellow from formation of a cuprous salt, and yields diphosphide of copper. (H. Rose.) In other respects, it exhibits the same characters as *d*.

Trombolite. Sp. gr. from 3·28 to 3·4; fractured conchoidal; colour yellowish-green inclining to emerald-green. (Breithaupt, *J. pr. Chem.* 15, 321.)

	Trombolite.		Plattner.
2CuO	80·0	42·69	39·2
PO^5	71·4	38·10	41·0 (nearly)
4HO	36·0	19·21	16·8
SiO^2,Al^2O^3			trace
$2CuO,PO^5+4Aq.$	187·4	100·00	97·0

f. Acid Phosphate.—The solution of *e* in aqueous phosphoric acid leaves on evaporation a green, gummy mass.

E. Pyrophosphate of Cupric Oxide, or Cupric Pyrophosphate.—Dissolves in aqueous pyrophosphate of soda; decomposed, by boiling with ordinary phosphate of soda, into ordinary phosphate of cupric oxide and pyrophosphate of soda. (Stromeyer.) ¶ Preparing by precipitating a cupric salt with pyrophosphate of soda. Amorphous, greenish-white powder, which becomes dark blue when dried at 100°, and assumes a lighter blue colour on ignition. Dissolves in mineral acids and ammonia, and likewise in pyrophosphate of soda. When boiled with caustic potash, it is resolved into cupric oxide and phosphate of potash. Sulphurous acid dissolves it without converting it into a cuprous salt, and the solution, when boiled, deposits it again in the crystalline state. The salt dried at 100° contains $2CuO,PO^5+2Aq$. The two atoms of water are given off on ignition. (Schwarzenberg, *Ann. Pharm.* 65, 156.)

	Anhydrous.		Schwarzenberg. *Amorphous.*	*Crystalline.*
2CuO	80·0	52·84	52·1	52·89
bPO^5	71·4	47·16	47·9	47·11
$2CuO,bPO^5$	151·4	100·00	100·0	100·00

F. Metaphosphate of Cupric Oxide, or Cupric Metaphosphate.—Formed by adding a solution of cupric nitrate to dilute phosphoric acid, evaporating and heating above 316°; whereupon it is deposited in the form of a bluish-white powder. Insoluble in water and dilute acids, but soluble in strong sulphuric acid.

			Maddrell.
CuO	40·0	35·9	35·7
PO^5	71·4	64·1	64·3
CuO, aPO^5	111·4	100·0	100·0

(Maddrell, *Ann. Pharm.* 61, 60.) ¶

Copper and Sulphur.

A. Disulphide of Copper, or Cuprous Sulphide.—Found in the form of *Copper-glance.*—*Formation.*—1. By triturating copper with sulphur. When 64 pts. (2 At.) of finely divided copper, obtained by reducing the carbonate by hydrogen, and 16 pts. (1 At.) of milk of sulphur are dried together over oil of vitriol, and triturated together in a mortar, so gently that no heat is produced by the friction, they combine as soon as a uniform mixture is attained, and form bluish disulphide, the combination being attended with a development of heat which raises the mass to redness. If the proportion of the copper to the sulphur be even slightly altered, the experiment fails, even though the mortar be warmed. If the mortar be warmed to 20° or 25°, it is not necessary to dry the powders previously, and moreover, flowers of sulphur may be used instead of milk of sulphur, only that longer trituration is necessary to induce combination. (Winkelblech, *Ann. Pharm.* 21, 34.) Sulphide of copper is also formed by triturating copper filings with sulphur and water.—2. Thin copper leaf burns with vivid inflammation in a glass flask in which sulphur has been heated till it volatilizes. 8 parts of copper filings mixed with 3 parts of pounded sulphur unite with incandescence when heated. The same compound is obtained by fusing together plates of copper and pounded sulphur, arranged in a crucible in alternate layers.—3. By igniting protoxide of copper with sulphur.—4. One hundred parts of dry cupric sulphate heated to whiteness in a crucible lined with charcoal, yield 47·6 parts of disulphide of copper, mixed with a few granules of the metal. (Berthier, *Ann. Chim. Phys.* 22, 236.)

Copper-glance belongs to the right prismatic system. *Fig.* 56 with the *p*-face; $t : u = 120° 12\frac{1}{2}'$; $u : u' = 60° 25'$; $a : u = 115° 50'$; $i : t = 115° 58'$. Cleavage imperfect, parallel to *u*. (Mohs, *Pogg.* 24, 428; Mitscherlich, *J. pr. Chem.* 19, 451.) The crystals of copper-glance were formerly regarded as belonging to the hexagonal system. Mitscherlich (*Pogg.* 24, 428), by fusing together large quantities of copper and sulphur, obtained regular octohedrons. Specific gravity of the native sulphide, from 5·695 to 5·735 (Mohs); of the artificial compound, 5·9775 (Karsten). Disulphide of copper, whether natural or artificial, is harder than gypsum, slightly malleable, of a blackish lead-grey colour, and much more easily fusible than copper.

Accordingly, 80 pts. (1 At.) Cu^2S should separate 312 pts. (3 At.) of lead =100 : 390. (Berthier, *Ann. Chim. Phys.* 89, 246.) Lead exerts no decomposing action on sulphide of copper when fused with it. (Karsten.) Disulphide of copper ignited with the protoxide is easily converted into sulphurous acid and metallic copper, or the dioxide. 1 At. Cu^2S and 2 At. CuO are completely converted into sulphurous acid and copper:

$$Cu^2S + 2CuO = 4Cu + SO^2.$$

With 4 At. CuO [6 At. according to Gmelin] the only products are sulphurous acid and cuprous oxide:

$$Cu^2S + 6CuO = 4Cu^2O + SO^2.$$

Any excess of disulphide of copper remains undecomposed. (Karsten, *Schw.* 66, 401.)—Metallic iron decomposes disulphide of copper, though very imperfectly, yielding copper containing iron, iron containing copper, and sulphide of copper and iron. Ferric oxide exerts but a slight decomposing action, and ferrous silicate none at all.

B. Protosulphide of Copper, or Cupric Sulphide.—Found in the form of *Indigo Copper* or *Blue Copper, Breithauptite.*—1. Precipitated on passing sulphuretted hydrogen through a cupric salt, in black flakes, which become greenish-black when dry and redden litmus. The specific gravity of the sulphide precipitated by sulphide of ammonium and dried out of contact of air at a temperature above 100°, is 4·1634. (Karsten.) —2. When finely pounded disulphide of copper is triturated in a mortar with cold strong nitric acid till the action ceases, and then washed, protosulphide of copper remains, in the form of a greenish-black powder. (Faraday, *Quart. J. of Sc.* 21, 183.)—Protosulphide of copper ignited out of contact of air, gives off half its sulphur and is converted into the disulphide. (Döbereiner, *Schw.* 17, 414.) When exposed to the air in the moist state, it is converted into sulphate of cupric oxide. (*Sch.* 30.) It dissolves in hot nitric acid, with separation of sulphur and formation of sulphuric acid. Hot concentrated hydrochloric acid dissolves it slowly, with evolution of sulphuretted hydrogen, precipitation of sulphur, and formation of acid hydrochlorate of cuprous oxide. From nitrate of silver-oxide, it throws down sulphide of silver. It does not dissolve in aqueous sulphurous acid, caustic potash, or alkaline hydrosulphates.

Native protosulphide of copper is found sometimes attached to and associated with copper pyrites,—massive, of specific gravity 3·8, soft, and of a bluish-black colour,—sometimes, in the fumaroles of Vesuvius, in the form of a sooty deposit or a black net-work like a spider's web. (Walchner, *Schw.* 49, 158; Covelli, *Ann. Chim. Phys.* 35, 105; also *Pogg.* 10, 494.)

				Walchner. Hans Baden.	Covelli. Vesuvius.
Cu	32	66·67		64·77	66
S	16	33·33		32·64	32
Fe				0·46	
Pb				1·05	
SO^3				trace	
CuS	48	100·00		98·92	98

C. Pentasulphide of Copper.—Aqueous pentasulphide of potassium forms with cupric salts a liver-coloured precipitate which turns black after drying, is not altered by exposure to the air, or by washing with

boiling water, and, when recently precipitated dissolves, in aqueous carbonate of potash, forming a brown solution. (Berzelius.)—According to Berzelius, bisulphide, tersulphide, and tetrasulphide of potassium give with cupric salts a precipitate of the same colour, likewise soluble in carbonate of potash, and consisting of a mixture either of CuS and CuS^5 or of CuS^2, CuS^3, and CuS^4.

D. Hyposulphite of Cuprous Oxide, or Cuprous Hyposulphite. —Formed by precipitating hyposulphite of lime with sulphate of cupric oxide, or by digesting it with carbonate of cupric oxide.—Colourless solution, having a sweet taste and turning blue in the air when supersaturated with ammonia. (Herschel.)

E. Sulphite of Cuprous Oxide, or Cuprous Sulphite.—1. Formed by digesting cupric oxide or its hydrate or carbonate with aqueous sulphurous acid. (Chevreul, Berthier.) The products of this reaction are soluble cupric sulphate and crystallized cuprous sulphite:

$$3CuO + 2SO^2 = CuO, SO^3 + Cu^2O, SO^2.$$

Ignited cupric oxide is but slowly acted on by sulphurous acid at ordinary temperatures; but on the application of heat, the decomposition goes on rapidly and is attended with the formation of a blue solution of cupric sulphate, and red crystalline scales of cuprous sulphite, amounting to eight parts for every ten of the cupric oxide used. Carbonate of cupric oxide dissolves readily and with effervescence in the cold acid, forming a green solution of cupric sulphite, which, slowly in the cold, more quickly in sunshine, and very rapidly if gently warmed, turns blue and deposits red scales. (Berthier.) Finely pounded Azure Copper-ore acts in the same manner as the artificial carbonate, but more slowly. (A. Vogel, *J. pr. Chem.* 30, 39.) Hydrated cupric oxide immersed in sulphurous acid is immediately converted into brown-red sulphite of cuprous oxide. (Böttger, *Ann. Pharm.* 39, 178.) 2. The same salt is precipitated on mixing aqueous sulphite of potash or soda with a warm solution of cupric sulphate or nitrate. (Chevreul.) To obtain fine crystals, strong potash-ley saturated in the cold with sulphurous acid, must be added to a solution of blue vitriol, the liquid filtered from the small quantity of cuprous sulphite which falls down, and the filtrate gently heated till the crystals begin to separate out. (Bourson, *Compt. rend.* 13, 111; also *J. pr. Chem.* 25, 399.)

Shining, cochineal-coloured, crystalline granules and scales.—When heated in a retort, they give off water and sulphurous acid, and leave a small quantity of cuprous oxide of a somewhat darker red colour. (Berthier.)—When boiled with water, they are resolved into sulphurous acid gas, cupric sulphate, cuprous oxide, and a small quantity of sulphide of copper. (Chevreul, *Ann. Chim.* 83, 181; also *Gilb.* 48, 185.) In the dry state, they do not alter by exposure to the air (Chevreul); but when moist, they are converted into a mixture of normal and basic sulphate of cupric oxide. (Berthier.) Sulphuric acid, even when cold and dilute, decomposes the crystals immediately, converting them into cupric oxide which dissolves, and dark red, finely divided metallic copper. They are scarcely soluble in water, but dissolve in sulphurous acid, hydrochloric acid, and ammonia. (Berthier, *N. Ann. Chim.* 7, 81.)

	Crystallized.				Chevreul.
Cu^2O	72		59·02		56·82
SO^2	32		26·23		32·18
2HO	18		14·75		11·00
$Cu^2O, SO^2 + 2Aq.$	122		100·00		100·00

¶ The composition of this red salt is variously stated by different chemists. Muspratt (*Ann. Pharm.* 50, 285), by passing sulphurous acid gas into water in which a small quantity of cupric oxide was suspended, and slowly evaporating the bright green solution thereby produced, obtained after a few days, large, fine, purple crystals, yielding a red powder: they were found to consist of $Cu^2O, SO^2 + Aq.$—Böttinger (*Ann. Pharm.* 52, 410), by mixing a solution of cupric sulphate with sulphite of ammonia containing but a small quantity of free sulphurous acid, obtained a dirty greenish-yellow precipitate, which, on the addition of a little sulphurous acid, was rapidly and easily converted into a beautiful green liquid. If, on the contrary, the sulphite of ammonia contained a sufficient quantity of free sulphurous acid, no precipitate was produced in the cold, the liquid merely acquiring a green colour. But on slowly heating either of these solutions to about 60°, a white salt separated out, which was found to be a double sulphite of cuprous oxide and ammonia. At a higher temperature, this salt is quickly converted into a red granular compound, which, when examined by the microscope, is found to consist of oblique four-sided prisms. The same red salt may be obtained immediately by heating a solution of blue vitriol with sulphite of ammonia containing free sulphurous acid, to the boiling point. Its composition, according to Böttinger, is as follows:—

					Böttinger.
$3Cu^2O$	216		56·55		56·28 to 56·06
$4SO^2$	128		33·93		34·44
4HO	36		9·52		9·28
$3Cu^2O, 4SO^2 + 4Aq.$	380		100·00		100·00

This salt, when boiled for a long time in the liquid, gives off sulphurous acid and becomes lighter in colour. In this state, Böttinger found it to contain 66·6 p. c. Cu^2O. Hence may be explained the discordant results obtained by different chemists in the analysis of this red salt.—According to Rammelsberg, its formula is $CuO, SO^2 + Cu^2O, SO^2 + HO$. ¶

F. Sulphite of Cupric Oxide, or Cupric Sulphite.—The green liquid obtained by dissolving carbonate of cupric oxide in cold aqueous sulphurous acid consists of this salt; it soon changes, however, especially when heated, into cuprous sulphite and cupric sulphate. (Berthier.)

G. Hyposulphate of Cupric Oxide, or Cupric Hyposulphate.—*a. Quadrobasic.*—Formed by mixing the aqueous solution of *b* with a small quantity of ammonia. Verdigris-coloured precipitate. Turns violet-juice green. Does not absorb carbonic acid from the air. When heated, it assumes first a dark green and then an ochre-yellow colour. Very sparingly soluble in water. (Heeren.)

	Quadrobasic.				Heeren.
4CuO	160		59·70		60·36
S^2O^5	72		26·86		27·35
4HO	36		13·44		12·29
$4CuO, S^2O^5 + 4Aq.$	268		100·00		100·00

b. Monobasic.—Preparation similar to that of the corresponding ferrous salt (p. 236). Rhombic prisms, having the lateral edges inclined at angles of about 108° and 72°, and with dihedral summits resting on the acute lateral edges. The crystals are slightly efflorescent, decrepitate violently when heated, and leave 52·69 per cent. of cupric sulphate. Very easily soluble in water, but insoluble in alcohol. (Heeren.)

	Monobasic.		Heeren.
CuO	40	27·03	26·43
S^2O^5	72	48·65	48·10
4HO	36	24·32	25·47
$CuO,S^2O^5+4Aq.$	148	100·00	100·00

H. Sulphate of Cupric Oxide, or Cupric Sulphate.—*a. Octobasic.*—Formed by mixing a solution of blue vitriol with a quantity of potash just sufficient to precipitate all the copper, but not to give the liquid an alkaline reaction—then washing and drying the precipitate.—Apple-green powder. Turns blue and gives off water when heated. 10·76 per cent. of water escapes at 149°, and 10·52 per cent. more between 149° and 260°; consequently, 6 atoms of water are more intimately united with the salt than the other six. The dehydrated salt, when placed in contact with water, regains its fine green colour and becomes heated. (Kane, *Ann. Chim. Phys.* 72, 269.)

			Kane.
8CuO	320	68·37	
SO^3	40	8·55	8·94
12HO	108	23·08	21·28
$8CuO,SO^3+12Aq.$	468	100·00	

b. Quadrobasic.—Occurs in the form of *Brochantite.* The hydrate and the recently-precipitated carbonate of cupric oxide are converted into this salt by immersion in a solution of blue vitriol. (Proust, *A. Gehl.* 6, 567.)—2. The same salt is also formed by precipitating a solution of blue vitriol with so small a quantity of potash or ammonia, that part of the solution shall remain undecomposed. (Proust, *Ann. Chim.* 32, 34; Berzelius, *Gilb.* 40, 300; Kühn, *Schw.* 60, 343.)—The precipitate carries down with it a quantity of sulphate of potash, which cannot be removed by washing. (Graham, *Ann. Pharm.* 29, 29.)—3. By boiling a solution of blue vitriol with a quantity of zinc-oxide not sufficient to throw down the whole of it. The precipitate is free from zinc. (Brunner, *Pogg.* 15, 479.)—4. The same salt is likewise precipitated from a solution of blue vitriol, supersaturated with ammonia and exposed to the air. (Kühn.)—5. It is also obtained by treating with water the green powder which remains on gently heating the sulphate of cupric oxide and ammonia. (Kane.)—Pale green powder.—Does not dissolve in water, or give up any of its sulphuric acid to that liquid. Undergoes no alteration at 100°; at a higher temperature, it gives off water, and is converted (after first turning olive-green) into a brown mixture of cupric oxide and monobasic cupric sulphate, which latter becomes hot by contact with water, and may be extracted by it; but if the solution thus formed be left to stand for some time in contact with the cupric oxide, the monobasic salt is reproduced. (Proust.) This salt gives off only one atom of water at the melting-point of lead. (Graham.) According to Kane, no water goes off below 149°, but at that temperature the whole is evolved; the

blue pulverulent residue absorbs water slowly from the air, but quickly when moistened, the combination being attended with evolution of heat, and the salt acquiring a bluish-green colour.

Brochantite.—Crystalline system the oblique prismatic. *Fig.* 55, together with the *y*-face. (Levy.) The Peruvian mineral is a pale green, earthy mass, sometimes of the hardness of soft sandstone, sometimes friable between the fingers, sometimes argillaceous. Boiling water extracts from it nothing but a small quantity of gypsum. When ignited and subsequently treated with water, it behaves like the artificial salt. Contains 27 per cent. of sand mixed with it. (Proust, *N. Gehl.* 2, 54.)—The mineral from Siebenbürgen resembles malachite in external appearance, but has a higher lustre and darker colour. Sp. gr. from 3·78 to 3·87. At a red heat, it gives off a small quantity of sulphurous acid together with water. Before the blowpipe on charcoal, it fuses and yields a button of copper. (Magnus, *Pogg.* 14, 141.)—Berthier (*Ann. Chim. Phys.* 50, 360) examined a similar compound from Mexico.

	Proust. *artif.*	Kane. *artif.*	Kühn. *artif.*	Brunner. *artif.*	Berzelius. *artif.*	Proust. *native.*	Magnus. *native.*	Berthier. *native.*
CuO	68	....	67·11	65·61	64·22	70	66·93	66·2
SO^3	18	16·81	18·36	22·61	21·28	19	17·43	16·6
HO	14	15·73	14·53	11·78	14·50	11	11·92	17·2
SnO^2	....	....	....	....	....	....	3·14	
PbO	....	....	....	....	....	....	1·05	
	100	....	100·00	100·00	100·00	100	100·47	100·0

The analytical results vary between the three following formulæ: *a.* $4CuO, SO^3 + 4\ Aq.$—*b.* $4CuO, SO^3 + 3\ Aq. = CuO, SO^3 + 3(CuO, HO)$.—*c.* $3CuO, SO^3 + 3\ Aq.$ — The calculations from these formulæ give the following per centages:

	At.	*a.*		At.	*b.*		At.	*c.*	
CuO	4	160	67·80	4	160	70·49	3	120	64·17
SO^3	1	40	16·95	1	40	17·62	1	40	21·39
HO	4	36	15·25	3	27	11·89	3	27	14·44
		236	100·00		227	100·00		187	100·00

Berzelius (*Jahresber.* 11, 176), on further examination of the salt precipitated by an insufficient quantity of potash, found that it contained not quite 4 At., but considerably more than 3 At. cupric oxide to 1 At. sulphuric acid; probably, therefore, a mixture of two basic salts.

c. Bibasic ?—When an aqueous solution of 125 pts. (1 At.) blue vitriol is digested for some months with 40 pts. (1 At.) of finely pulverized cupric oxide, the liquid becomes completely decolorized, and a green powder insoluble in water is produced. (Thomson, *Ann. Phil.* 17, 244.)

A concentrated solution of blue vitriol digested with cupric oxide takes up a certain quantity of that substance, and yields four-sided prisms terminated by four-sided pyramids. (Leblanc, *J. Phys.* 55, 301.) Any pale green precipitate [of quadrobasic salt] that may be formed during the digestion, disappears again on the addition of more blue vitriol solution. The crystals are distinguished from those of blue vitriol, not only by their form, but likewise by their blue colour. (Hünefeld, *Schw.* 50, 342.)

d. Monobasic.—Sulphate of Copper, Blue Vitriol, Copper-vitriol, Cyprian Vitriol.—Occurs here and there as a modern natural formation.

Formation.—1. When copper is immersed for half a year in an aqueous solution of sulphurous acid contained in a close vessel, cupric sulphate and sulphide of copper are formed, and the acid loses its odour. (Barruel.)

$$2Cu + 2SO^2 = CuO, SO^3 + CuS.$$

2. Copper heated with oil of vitriol yields cupric sulphate and sulphurous acid gas:

$$Cu + 2SO^3 = CuO, SO^3 + SO^2;$$

part of the sulphurous acid, however, acts on the copper as in (1), so that the cupric sulphate produced is mixed with sulphide of copper. This sulphide of copper appears to constitute the black powder which Berzelius (*Ann. Chim. Phys.* 2, 228) supposed to consist of cuprous sulphate. Even at ordinary temperatures, sulphuric acid kept in contact with copper in a close vessel slowly produces cupric sulphate, with simultaneous formation of sulphide of copper. (Barruel, *J. Pharm.* 20, 15.)—Copper-turnings and oil of vitriol placed together in a vessel completely filled with the liquid, and closed, exhibit the following phenomena:—At the end of one week, a pale rose-coloured liquid; after 3 weeks, the liquid decolorized, the copper still bright; after 8 weeks, a small quantity of brownish powder, consisting of sulphide of copper, deposited at the bottom of the vessel; this powder continues to increase in quantity up to the fifth month, and finally, transparent and colourless crystals of anhydrous cupric sulphate, which form a blue solution in water, are deposited on the sides of the vessel. After the lapse of six months, the colourless liquid emits a strong odour of sulphurous acid, and turns blue when mixed with water, showing that it contains anhydrous cupric sulphate dissolved in oil of vitriol. Hence it appears that the sulphuric acid is slowly decomposed, yielding cupric sulphate and sulphurous acid; and the latter is at first wholly expended in forming (according to 1) sulphide of copper and cupric sulphate with the rest of the copper. (Barruel.) Even a mixture of 60 drops of oil of vitriol with 6 ounces of water inclosed with copper in a bottle for 69 days, yields a liquid which is colourless, but turns blue on the addition of ammonia, while the copper becomes covered with black cupric oxide [sulphide?]. (J. Davy, *N. Edinb. Phil. J.* 8, 229.)—3. If the air has access to the liquid, the copper gradually takes up oxygen from it, and dissolves in the sulphuric acid, whether it be dilute or moderately concentrated.—4. Disulphide of copper heated in the air forms cupric sulphate and free cupric oxide. Even at ordinary temperatures, many copper-ores containing sulphide of copper, yield blue vitriol by contact with air and water.

Preparation.—1. By heating 1 At. copper with at most 2 At. oil of vitriol till the residue is dry—then exhausting with hot water, filtering from the copper and sulphide of copper, and cooling the filtrate till it crystallizes. 32 pts. copper require 98 oil of vitriol; which may be diluted with one-third of its weight of water.—2. By heating 3 At. copper with 3 At. oil of vitriol and 1 At. nitric acid together with water:

$$3Cu + 3SO^3 + NO^5 = 3(CuO, SO^3) + NO^2.$$

The salt, when dissolved in water, has an astringent metallic taste and reddens litmus.—At a strong red heat, it gives off all its acid, partly in the form of sulphurous acid and oxygen gas (Gay-Lussac), partly as anhydrous sulphuric acid. (Bussy.)—By hydrogen at a red heat, it is reduced to the state of metallic copper. (Arfvedson, *Pogg.* 1, 74.) Heated to dull redness with excess of charcoal, it gives off carbonic and sulphurous acid gases in exactly equal volumes, while copper free from sulphur remains behind:

$$CuO, SO^3 + C = Cu + SO^2 + CO^2.$$

At a higher temperature, a violent disengagement of gas takes place, and a mixture of metallic copper and sulphide of copper remains, because the sulphurous acid gas evolved in the inner and less heated part of the mixture, acts upon the copper and charcoal in the outer portions, in such a manner as to form sulphide of copper and carbonic acid. (Gay-Lussac, *J. pr. Chem.* 11, 69.)—When gently heated in a stream of phosphuretted hydrogen gas, the salt gives off water and sulphurous acid, turns brown, and is finally converted into a black mixture of phosphide of copper and variable quantities of the disulphide. (H. Rose, *Pogg.* 24, 330.)—The aqueous solution added in excess, colours pentasulphide of antimony brown, and if boiled for some time with that substance, yields a mixture of black sulphantimoniate of copper and white antimonic acid. (Rammelsberg, *Pogg.* 52, 241):

$$15(CuO, SO^3) + 8SbS^5 = 5(3CuS, SbS^5) + 3SbO^5 + 15SO^3.$$

(For the decomposing action of zinc on the aqueous solution, see p. 409.) —Crystallized blue vitriol dissolves in aqueous hydrochloric acid with a reduction of temperature amounting to about 17°, and forms a green liquid, which, when formed by the action of at least 1 atom of hydrochloric acid on 1 atom of blue vitriol, yields, on evaporation and cooling, crystals of pure hydrated chloride of copper, the whole of the sulphuric acid remaining in the mother-liquid in the free state. No sulphate of copper crystallizes out unless the proportion of hydrochloric acid is less than one atom. If, however, the crystallized chloride of copper is left for some time exposed to the air in contact with the mother-liquid which contains the sulphuric acid, crystals of blue vitriol are reproduced [in consequence of the evaporation of the hydrochloric acid?].—Cupric sulphate containing no water, or only 1 atom, absorbs rapidly and with great evolution of heat, a quantity of hydrochloric acid gas amounting to nearly one atom: no water is set free, but a dark chocolate-coloured mass is formed, which rapidly gives off all its hydrochloric acid at a higher temperature, but when dissolved in water, yields crystals of chloride of copper and a mother-liquid containing free sulphuric acid. When hydrochloric acid gas is passed over ordinary blue vitriol (containing 5 At. water) in the state of powder, great heat is evolved, water is given off, and the salt rapidly absorbs rather more than 1 atom of hydrochloric acid (in consequence of the water being set free) and forms a grass-green mass—brown where the salt has been most strongly heated—which fumes strongly from evolution of hydrochloric acid, and is very acid and deliquescent. (Kane, *Phil. Mag. J.* 8, 353; also *Ann. Pharm.* 19, 1.)

In the humid way, cupric sulphate resolves itself with sal-ammoniac into sulphate of cupric oxide and ammonia, and protochloride of copper (A. Vogel, Karsten); with common salt, into sulphate of cupric oxide [and soda?] and protochloride of copper (Boussingault, *Ann. Chim. Phys.*

51, 390); with nitrate of potash or soda, into sulphate of cupric oxide and potash or soda, and nitrate of cupric oxide (Karsten).

Combinations with Water.—When cupric sulphate which has been dehydrated by heat is moistened with water, the water is absorbed, the temperature rises 135°, and the salt acquires a blue colour. (Graham.)—When exposed to moist air for 3 days, it takes up the 5 atoms of water belonging to ordinary blue vitriol. (Brandes, *Schw.* 51, 436.)

α. *Mono-hydrated.*—Remains, when the penta-hydrated salt is heated in vacuo to 38°, in the form of a greenish-white, friable mass, which, at a temperature between 221° and 242°, gives off its last atom of water and becomes white. (Graham, *Phil. Mag. J.* 6, 419.)

β. *Bi-hydrated.*—The penta-hydrated salt kept for 7 days in vacuo over oil of vitriol at a temperature between 19° and 21°, loses such a quantity of water, that 17·336 parts (nearly 2 At.) of water remain combined with 80 parts (1 At.) of the anhydrous salt.

γ. *Penta-hydrated.*—The ordinary form of cupric sulphate.—Separates from the aqueous solution, on cooling, in azure-blue, transparent crystals belonging to the doubly oblique prismatic system. *Figs.* 121, 122, 123, and other forms. $y : u = 109° 32'$; $y : v = 128° 37'$; $u : v = 124° 2'$; $u : w = 150° 20'$; $u : w = 126° 11'$, &c. Cleavage indistinct, parallel to *y*, *u*, and *v*. (Hauy.) Sp. gr.=2·274. (Kopp.) The crystals effloresce on the surface in dry air. They dissolve in 3 parts of cold and ½ pt. of boiling water. One part of the crystals dissolves at 4° in 3·32 pts., at 19° in 2·71, at 31° in 1·84, at 37·5° in 1·7, at 50° in 1·14, at 62·5° in 1·27 [!], at 75° in 1·07, at 87·5° in 0·75, at 100° in 0·55, and at 104° in 0·47 parts of water. (Brandes & Firnhaber.) The crystals dissolve at 17·5° in 2·412 parts of water, forming a solution whose density is 1·182. (Karsten.) A solution saturated at 8° has a density of 1·17. (Anthon.) Glacial acetic acid completely precipitates blue vitriol from its aqueous solution. (Persoz.)

			Thomson.	Berzelius.	Proust.	Kirwan.
CuO	40	32	32	32·13	32	40
SO^3	40	32	32	31·57	33	31
5HO	45	36	36	36·30	35	29
$CuO,SO^3+5Aq.$	125	100	100	100·00	100	100

The native blue vitriol from Chili contains small quantities of the sulphates of ferric oxide, lime, magnesia, and alumina. (H. Rose, *Pogg.* 27, 318.)

The colourless solution of anhydrous cupric sulphate in oil of vitriol acquires a beautiful violet or violet-blue colour by contact with nitric oxide gas. The liquid is immediately decolorized by dilution with water, and likewise by oxidizing agents, such as hyponitric acid, nitric acid, nitrates, and manganic sulphate, but not by nitrites. (Desbassins de Richemont, *J. Chim. Méd.* 11, 504.)—Jacquelain (*Compt. rend.* 14, 643) was unable to produce this violet compound, and suspects the presence of green vitriol in the blue vitriol used by Desbassins. But the colour is quite different, and is produced even in pure blue vitriol diffused through rectified sulphuric acid. (Gm.)

I. *Carbosulphide of Copper ?*—When bisulphide of carbon is passed over red-hot copper, the carbon, according to Cluzel, is separated and deposited on the surface of the copper; but according to Berzelius, *Thénard* & Vauquelin, the bisulphide of carbon combines as a whole

with the copper, forming a shining black substance, which, when treated with nitric acid, leaves a residue of charcoal.

K. Sulphocarbonate of Copper.—Cupric salts yield with sulphocarbonate of calcium a dark brown precipitate, soluble and forming a dark brown solution in excess of sulphocarbonate of calcium, black after drying; when distilled, it first gives off bisulphide of carbon, then sulphur, and leaves disulphide of copper. (Berzelius.)

L. Cuprous Hyposulphophosphite.—*a.*—*Bibasic.*—$2Cu^2S,PS$.—Remains in the form of a liver-coloured powder, when the compound $2Cu^2S,PS^3$ is ignited in a retort.

b. Monobasic.—Disulphide of copper does not combine with protosulphide of phosphorus when the two are heated together; but when the following compound (M) is ignited in a retort, PS is first evolved, then a sulphide of phosphorus richer in sulphur, and there remains a liver-coloured powder$=Cu^2S,PS$, which assumes a lighter colour when rubbed, and if ignited in the air, is converted, with faint glow (but without phosphorus-flame), into sulphurous acid gas and a black, oxidized mass.—The same compound is produced by the action of PS on dichloride of copper dissolved in ammonia. (Berzelius.)

M. Cupric Hiposulphophosphite.—Protosulphide of copper precipitated by sulphuretted hydrogen from a solution of blue vitriol, then washed with water freed from air by boiling, and dried in vacuo, is treated with protosulphide of phosphorus in the bulb-apparatus, as described in the preparation of sulphide of phosphorus and zinc (p. 26). Combination then takes place, attended with so great a development of heat, that the excess of sulphide of phosphorus is almost instantly distilled off; what remains is afterwards expelled by the application of a very gentle heat. The compound is left in the tube till it is cold; it contains a few granules of uncombined sulphide of copper, which are harder than the rest of the mass.—Black-brown, becoming lighter when pulverized.—When heated in the air, it burns with a phosphorus-flame, and leaves a light liver-coloured powder. When distilled, it behaves in the manner mentioned under L, *b*.—Insoluble in dilute hydrochloric acid, but dissolves to a slight extent in that acid when hot and concentrated, forming a deep yellow solution, from which it is completely precipitated in dark brown flakes by water, so that the liquid, after dilution, no longer retains a trace of copper. (Berzelius, *Ann. Pharm.* 46, 252.)

					Berzelius.
Cu	32·0	....	33·54	.....	37·57
P	31·4	....	32·92	.....	30·60
2S	32·0	....	33·54	.....	30·16
CuS, PS	95·4	....	100·00	.....	98·33

The compound analyzed by Berzelius, being mixed with a small quantity of free sulphide of copper, the proportion of phosphorus came out rather too small, and that of copper rather too great. (Berzelius.)

N. Cuprous Sulphophosphite. — *Bibasic.* — Bisulphide of copper precipitated from a solution of blue vitriol in excess of ammonia by soda-liver of sulphur, is washed, dried in vacuo, and treated with protosulphide of phosphorus, in the bulb-apparatus above mentioned (p. 26). Com-

bination takes place in this case also, with great evolution of heat. The excess of sulphide of phosphorus is driven off by a very gentle heat, a stream of hydrogen being passed through the apparatus all the time. Deep yellow powder. Heated in a retort to commencing redness, it gives off 2 atoms of sulphur, and leaves the compound L,a($2Cu^2S,PS$). May be set on fire in the air, and burns with a faint phosphorus-flame, being converted into a shining mass, which smells of sulphurous acid. (Berzelius.)

					Berzelius.
4Cu	128·0	....	53·47	.....	51·54
P	31·4	....	13·11	.....	13·09
5S	80·0	....	33·42	.....	35·17
$2Cu^2S,PS^3$	239·4	....	100·00	.....	99·80

The excess of sulphur obtained in the analysis proceeds from the admixture of a small quantity of $2CuS,PS^5$. (Berzelius.)

O. Cupric Sulphophosphate.—*a. Octobasic.*—Remains in the form of a yellow powder, on gently heating the bibasic compound, *b.* (Berzelius.)

8Cu	256·0	....	51·67	.....	52·05
P	31·4	....	6·34	.....	7·27
13S	208·0	....	41·99	.....	40·68
$8CuS,PS^5$	495·4	....	100·00	.....	100·00

b. Bibasic.—$2CuS,PS^5$.—Formed by gently heating 2 atoms of CuS,PS with 4 atoms of sulphur, 1 atom of PS volatilizing.

$$2(CuS,PS) + 4S = 2CuS,PS^5 + PS.$$

If, however, the heat rises a little too high, PS^5 is given off as well as PS, and the compound O,a remains. (Berzelius, *Ann. Pharm.* 46, 278.)

Copper and Selenium.

A. Diselenide of Copper, or Cuprous Selenide.—Found native. Formed by heating copper with selenium, the combination being attended with ignition; or by igniting the protoselenide in a close vessel. Dark steel-grey; has a close fracture, and fuses at a temperature considerably below redness. When heated in the air for a long time, it gives up only a portion of its selenium, emitting an odour of horse-radish, and leaving grey, brittle, easily fusible copper. (Berzelius.)

					Berzelius. Smaland.
2Cu	64	....	61·54	.....	64
Se	40	....	38·46	.....	40
Cu^2Se	104	....	100·00	.....	100

B. Protoselenide of Copper, or Cupric Selenide.—By precipitating blue vitriol with seleniuretted hydrogen. Black flakes, which become dark grey in drying, and acquire the metallic lustre by pressure. Gives off half its selenium on distillation. (Berzelius.)

C. Cuprous Selenite.—By digesting hydrated cuprous oxide with aqueous selenious acid. White powder, insoluble in water. (Berzelius.)

D. CUPRIC SELENITE.—*a. Basic.*—By precipitating blue vitriol with selenite of ammonia containing excess of ammonia. Pistachio-green, becoming black when heated, and giving off first the water, and then the whole of the acid, with intumescence. Insoluble in water, but soluble in ammonia.

b. Monoselenite.—On mixing a warm aqueous solution of blue vitriol with biselenite of ammonia, bulky, curdy, yellowish flakes are produced, which are quickly converted (slowly in the cold) into small, silky, greenish-blue crystals. When heated, they give off water, and become liver-coloured; then fuse, turn black, and give off all their water with ebullition. Insoluble in water and in aqueous selenious acid. (Berzelius.) ¶ According to Muspratt (*Chem. Soc. Qu. J.* 2, 66), this salt acquires a bright blue colour when dried over oil of vitriol.

				Muspratt.	
$3CuO$	120	40·40		40·55	
$3SeO^2$	168	56·56		56·03	
HO	9	3·04		3·42	3·18
$3(CuO,SeO^2)+Aq.$	297	100·00		100·00	¶

E. CUPRIC SELENIATE.—Crystals isomorphous with those of the sulphate. (Mitscherlich.)

COPPER AND IODINE.

A. DINIODIDE OF COPPER, or CUPROUS IODIDE.—1. Formed by heating finely divided copper with iodine.—2. By precipitating a solution of dichloride of copper in hydrochloric acid with iodide of potassium. (Sarphati.) If the hydrochloric acid is in too great excess, a small portion of iodide of copper remains dissolved in it; and if the quantity of hydrochloric acid is too small, dichloride of copper may be precipitated together with the iodide. (Buchner, *Repert.* 78, 8.)—3. By precipitating a dissolved cupric salt with iodide of potassium, half of the iodine being set free:

$$2(CuO,SO^3)+2KI = 2(KO,SO^3)+Cu^2I+I.$$

The precipitate must be washed with alcohol, to free it from adhering iodine. (Berthemot.) By precipitating a solution of cupric sulphate in a sufficient quantity of aqueous sulphurous acid, with iodide of potassium. (Duflos, *Ann. Pharm.* 39, 253.)

$$2(CuO,SO^3)+KI+SO^2 = KO,3SO^3+Cu^2I.$$

5. By precipitating the aqueous solution of 1 At. cupric sulphate, and at least 1 At. ferrous sulphate, with iodide of potassium. (Soubeiran, *J. Pharm.* 13, 427.)

$$2(CuO,SO^3)+2(FeO,SO^3)+KI = KO,SO^3+Fe^2O^3,3SO^3+Cu^2I.$$

According to Soubeiran, iodide of copper obtained by precipitation and dried at 40°, contains 4 per cent. of water, so that its formula is $Cu^2I+Aq.$, or $Cu^2O,HI.$—6. Becquerel, by the electrolytic process, (I,401) obtained iodide of copper in octohedrons.

Iodide of copper obtained by precipitation is a brownish-white powder. When heated, it gives off 4 per cent. of water, and at a red heat fuses into a brown mass, which yields a green powder. (Soubeiran.) It is but

imperfectly decomposed by ignition in a stream of hydrogen gas. (H. Rose, *Pogg.* 4, 110.) When ignited with peroxide of manganese, it is resolved into iodine vapour and cupric oxide. (Soubeiran.) With nitric acid, it yields vapour of iodine, nitric oxide gas, and cupric nitrate; and with oil of vitriol, it yields iodine vapour, sulphurous acid gas, and cupric sulphate. (Soubeiran.)

$$Cu^2I + 4SO^3 = 2(CuO,SO^3) + I + 2SO^2.$$

Iodide of copper boiled in water, with zinc, tin, or iron, yields metallic copper and a dissolved iodide of the other metal. (Berthemot, *J. Pharm.* 14, 614.) Aqueous fixed alkalis form metallic iodides and separate dioxide of copper; a similar reaction is produced by carbonate of potash or soda, carbonic acid being likewise evolved. No decomposition is produced by carbonate of baryta, strontia, or lime, or by alumina. (Berthemot, *comp.* II. 250.)

2Cu	64		33·68
I	126		66·32
Cu^2I	190		100·00

B. Iodate of Cupric Oxide, or Cupric Iodate.—Iodic acid and iodate of soda, mixed with blue vitriol and left over night, form a white precipitate. (Pleischl.) Iodate of soda precipitates cupric salts only when highly concentrated; it then forms a bluish-green precipitate. The salt is best prepared by dissolving hydrated cupric oxide in dilute iodic acid. At 200°, it loses 7·07 per cent. of water; when more strongly heated in a retort, it gives off oxygen gas and iodine vapour, and leaves cupric oxide free from iodine. It dissolves in hydrochloric acid, with evolution of chlorine; and on the addition of ammonia, iodide of nitrogen is precipitated. It dissolves in 302 parts of water at 15°, in 154 parts of boiling water, and easily in ammonia, forming a dark blue solution. (Rammelsberg, *Pogg.* 44, 569.)

C. Periodate of Cupric Oxide, or Cupric Periodate.—Monobasic periodate of soda yields, with cupric nitrate, a siskin-green precipitate, which dissolves in dilute nitric acid, and becomes yellowish when heated. (Benckiser, *Ann. Pharm.* 17, 260.)

Copper and Bromine.

A. Dibromide of Copper, or Cuprous Bromide.—Copper does not combine with bromine at ordinary temperatures, but on the application of heat, combination takes place: — 1. When bromine is placed at the sealed end of a glass tube, the upper part of the tube filled with fine copper wire, and the copper heated to dull redness, combination takes place, attended with vivid incandescence. The protobromide which mixes with the mass is dissolved out by water. On dissolving the product in aqueous hydrobromic acid, any copper which may remain uncombined is left behind, and the dibromide may be precipitated from the solution by water. (Löwig.) Another mode of preparation is to heat thin, rolled-up copper-foil in a flask, at the bottom of which some bromine is placed, and when combination attended with ignition is set up, to drop more bromine in, till the whole of the copper disappears. In this manner, dibromide of

copper is obtained in the form of a fused mass. (Berthemot, *Ann. Chim. Phys.* 44, 385; also *J. Pharm.* 16, 651.)—2. By igniting protobromide of copper. (Rammelsberg.)

By precipitation: white powder; after fusion: greyish-brown mass (Löwig); greenish-brown mass, having a crystalline fracture, and translucent when in thin laminæ. (Berthemot.) Fuses at a red heat, but does not volatilize if heated in close vessels, and with difficulty in an open vessel. (Löwig.) In a close vessel, it may be heated strongly without decomposition; but when heated in the air, it gives off vapours which impart a green colour to the flame of alcohol, and leaves a residue of cupric oxide. (Berthemot.) Dissolves in nitric acid, with evolution of nitric oxide. (Löwig.) Dissolves without decomposition in aqueous hydrobromic or hydrochloric acid. Dissolves in ammonia, but not in water. Not decomposed by boiling oil of vitriol or acetic acid. (Berthemot.)

					Berthemot.
2Cu	64·0	....	44·94	....	44·7
Br	78·4	....	55·06	....	55·3
Cu^2Br	142·4	....	100·00	....	100·0

Hydrobromate of Dibromide of Copper, or Acid Hydrobromate of Cuprous Oxide.—Dibromide of copper forms a colourless solution with concentrated hydrobromic acid. This solution yields, with green vitriol, a precipitate of metallic copper.

$$Cu^2Br + 3(FeO,SO^3) = 2Cu + FeBr + Fe^2O^3,3SO^3.$$

From a solution of protobromide of mercury, it throws down dibromide of mercury, and from a solution of chloride or bromide of gold, it precipitates metallic gold. Water decomposes it, throwing down dibromide of copper.

B. Aqueous Cuproso-cupric Bromide, or Hydrobromate of Cuproso-cupric Oxide.—When an aqueous solution of protobromide of copper is slowly evaporated, it gives off bromine, and is converted into a dark brown liquid, which, on the addition of water, recovers its original green colour, and yields a precipitate of dibromide of copper.

C. Protobromide of Copper, or Cupric Bromide.—Formed by evaporating the solution of cupric oxide in aqueous hydrobromic acid, and fusing the residue at a gentle heat. (Löwig.) The residue is iron-black, like plumbago. (Berthemot.) If the solution be left to evaporate in vacuo over oil of vitriol, anhydrous shining crystals are obtained, resembling iodine in appearance. (Rammelsberg, *Pogg.* 55, 246.)—According to Berthemot, protobromide of copper gives off half its bromine even below a red heat; according to Rammelsberg, it gives off 36·8 per cent., and leaves dibromide of copper.

Cu	32·0	.....	28·99
Br	78·4	.....	71·01
CuBr	110·4	.....	100·00

Hydrated Protobromide of Copper, or *Hydrobromate of Cupric Oxide.*—The emerald-green solution of cupric bromide in water, or of cupric oxide in aqueous hydrobromic acid, or of copper in a mixture of hydrobromic and nitric acids, becomes brown on evaporation, and yields right

COPPER AND CHLORINE.

A. DICHLORIDE OF COPPER, or CUPROUS CHLORIDE.—Boyle's *Resina Cupri*.—1. Copper filings and copper foil introduced into chlorine gas at ordinary temperatures, burn with a red light, and form dichloride and protochloride of copper. (J. Davy, *Schw.* 10, 312.) Copper reduced from the carbonate by hydrogen gas, burns in chlorine at ordinary temperatures with a white flame. (Osann.)—2. Copper heated with protochloride of mercury, yields vapour of mercury and dichloride of copper. (Boyle.) The decomposition takes place most readily with 1 pt. copper to 2 pts. corrosive sublimate. (J. Davy.) More exactly, 64 pts. (2 At.) copper and 136 pts. (1 At.) corrosive sublimate.—3. A plate of copper immersed in hydrochloric acid in a flask containing air, becomes covered with white tetrahedrons of dichloride of copper. (Proust.)—4. The compound may also be formed by agitating copper-filings with a solution of the protochloride in a close vessel (Proust):

$$CuCl + Cu = Cu^2Cl.$$

5. By precipitating the sulphate, hydrochlorate, nitrate or acetate of cupric oxide, with aqueous protochloride of tin, or by treating the hydrate or carbonate of cupric oxide with protochloride of tin dissolved in hydrochloric acid. (Proust):

$$2CuCl + SnCl = Cu^2Cl + SnCl^2.$$

6. By treating aqueous protochloride of copper with phosphorus, ether, sugar, &c.—7. By heating the protochloride in a retort for a considerable time; digesting the residue with water for several days with the retort closed, to dissolve out the undecomposed protochloride; and pouring off the resulting solution; the residue consists of dichloride. (Proust.)—8. By agitating pulverized dioxide of copper with hydrochloric acid in a close vessel. (Proust, Chenevix.)

When obtained by precipitation, it presents the form of a white crystalline powder, which acquires a dingy violet and blackish-blue tint by exposure to sunlight. (Proust.) Crystallizes from its solution in hot, concentrated, hydrochloric acid in white tetrahedrons (Proust), which turn bluish when exposed to light. (Mitscherlich, *J. pr. Chem.* 19, 449.) According to J. Davy, it separates in olive-green prisms. Fuses somewhat below a red heat, and when slowly cooled, solidifies in a translucent, light yellow mass (greyish-white; Proust); the residue obtained by rapid cooling is of a dark brown colour, and confused texture. (J. Davy.) Specific gravity of the melted mass = 3·677. (Karsten.) (As, however, it was obtained by fusion of the protochloride, it may perhaps have contained some of that compound; Gm.) In close vessels it does not volatilize, even when very strongly heated, but if heated in the air, it goes off in white vapours. (J. Davy.)

			J. Davy.
2Cu	64·0	64·38	64
Cl	35·4	35·62	36
Cu^2Cl	99·4	100·00	100

Or:		Berzelius.	Gay-Lussac.
Cu^2O	72·0	73·58	72·97
Cl − O	27·4	26·42	27·03
	99·4	100·00	100·00

When heated to redness in a stream of hydrogen, it is converted into metal and hydrochloric acid gas; in an atmosphere of phosphuretted hydrogen, it yields one-sixth phosphide of copper and hydrochloric acid gas. (H. Rose, *Pogg.* 4, 110; 6, 205.) With iron-filings under water, it yields metallic copper and soluble protochloride of iron. (Proust.) Ferrous sulphate added to the solution of dichloride of copper in hydrochloric acid, throws down metallic copper. (Proust.)—Dichloride of copper turns yellow when boiled with water; but the decomposition is not complete. (Proust.) With fused hydrate of potash, or the aqueous solution of potash, it yields dioxide of copper and chloride of potassium. (Proust.)—When exposed to the air in the dry state, it slowly attracts moisture and turns green; in the moist state, it is quickly converted into a green mass. (Proust.) With nitric acid, it forms first a violet, and then a blue solution, the action being attended with great rise of temperature and violent evolution of nitric oxide. (Proust.) A mixture of dichloride of copper and oil of vitriol assumes a faint violet colour when covered with a thin layer of fuming nitric acid. (Gm.) The hydrochloric acid solution of dichloride of copper imparts a blue colour to molybdic acid, decolorizes recently precipitated Prussian blue, throws down calomel from a solution of corrosive sublimate, and metallic gold from a solution of gold. (Proust.)—Dichloride of copper does not dissolve in water, or in dilute sulphuric acid; but dissolves without colour in strong hydrochloric acid, in aqueous ammonia, and in solution of common salt.

Aqueous Hydrochlorate of Cuprous Chloride, or *Acid Hydrochlorate of Cuprous Oxide.*—Formed by dissolving dichloride of copper in strong hydrochloric acid; or by agitating the acid in a close vessel with dioxide of copper, or with a mixture of the protoxide and excess of metallic copper; or by agitating copper-filings with a solution of the protochloride strongly supersaturated with hydrochloric acid; or by mixing the same solution with ether and exposing it to the sun's rays.—The colourless liquid prepared hot, deposits crystals of dichloride of copper on cooling. The solution, when mixed with a considerable quantity of water, deposits the greater part of the dichloride in the form of a white powder. (Proust, *Scher. J.* 8, 490; also *A. Gehl.* 6, 573.) Small quantities of ammonia added to the solution, produce transparent cubes of dichloride of copper and ammonium, which dissolve in a larger quantity of ammonia, forming a colourless liquid which turns blue on exposure to the air. Fuming nitric acid imparts to the solution, a dark greenish-brown colour, which afterwards changes to yellow, with evolution of nitrous gas. (Gm.)

B. Cupric Oxide with Cuprous Chloride.—$Cu^2Cl, 2CuO$.—The residue obtained by heating cupric oxychloride ($CuCO, 3CuO$). Proust.

C. Aqueous Cuproso-cupric Chloride, or Hydrochlorate of Cuproso-cupric Oxide.—Found by exposing the solution of cuprous oxide in excess of hydrochloric acid to the air; by mixing the same solution with a solution of protochloride of copper; or by agitating the latter with a small quantity of copper-filings.—Dark brown liquid. (Proust.)

D. Protochloride of Copper, or Cupric Chloride.—1. Formed by the combustion of copper in chlorine gas.—2. Dichloride of copper immersed in chlorine gas is slowly converted into the protochloride.—3. By heating the mono-hydrochlorate of cupric oxide somewhat above 200°.

Prepared by (1) it forms a brown sublimate, by (3), a brownish-yellow powder. Fusible. Has a caustic metallic taste. At a red heat, it gives off half its chlorine, and is converted into the dichloride. Heated in a current of phosphuretted hydrogen, it yields hydrochloric acid gas and triphosphide of copper. Fused with phosphorus, it forms chloride of phosphorus and phosphide of copper. (H. Rose, *Pogg.* 27, 117.)—Not decomposed by anhydrous sulphuric acid at ordinary temperatures. (H. Rose, *Pogg.* 38, 121.)—Oil of vitriol does not decompose it at ordinary temperatures, but completely when heated, hydrochloric acid being evolved. (A. Vogel.)—From the aqueous solution, phosphorus throws down dichloride of copper, and forms phosphoric acid (Boeck); the same precipitate is likewise produced by mercury, with formation of dichloride of mercury; by silver, with formation of chloride of silver, black at first but afterwards white (Wetzlar, *Schw.* 52, 475); and by protochloride of tin, with formation of bichloride of tin. Dichloride of copper is also precipitated on boiling the aqueous solution with sugar, and partly remains dissolved in the hydrochloric acid, produced by the reaction (A. Vogel); a solution of protochloride of copper mixed with ether and exposed to the sun's rays loses its colour, and on the addition of water yields a precipitate of the dichloride. (Gehlen, *A. Gehl.* 3, 570.) Heated in a current of olefiant gas, protochloride of copper yields a mixture of copper and dichloride of copper. (Wöhler.)

The reaction will be more fully described under the head of *Olefiant gas.*

			J. Davy.
Cu	32·0	47·48	47
Cl	35·4	52·52	53
CuCl	67·4	100·00	100

Or:			Berzelius.	Gay-Lussac.
CuO	40·0	59·35	59·79	62·05
Cl—O	27·4	40·65	40·21	37·95
	67·4	100·00	100·00	100·00

Hydrated Protochloride of Copper, or *Mono-hydrochlorate of Cupric Oxide.*—1. Protochloride of copper, when exposed to the air, turns green, and finally deliquesces to a green liquid.—2. The same compound is formed when copper immersed in hydrochloric acid is exposed to the air for a considerable time. The dichloride of copper and quadrobasic hydrochlorate formed at first, are converted, by longer action of the air and of hydrochloric acid, into a green solution of protochloride of copper.—3. By dissolving copper in aqua-regia.—4. By dissolving cupric oxide or carbonate in hydrochloric acid. The solution of cupric oxide in concentrated hydrochloric acid is attended with great development of heat. The emerald-green solution, when evaporated and cooled, yields green, right-angled four-sided prisms. These crystals fuse when gently heated, giving off water, and being converted into anhydrous protochloride of copper. (Proust.) At 100°, they turn brown, and give off the greater part of their water, but they do not part with the whole, which amounts to 21·53 per cent., till they are raised to a much higher temperature. (Graham, *Ann. Pharm.* 29, 31.) Cold oil of vitriol likewise abstracts water from them, and converts them into the brown anhydrous protochloride, which it does not dissolve or decompose. (A. Vogel.) The crystals deliquesce in the air.

					Graham.
Cu	32·0	....	37·47	.....	78·47
Cl	35·4	....	41·45		
2HO	18·0	....	21·08	.....	21·53
CuCl + 2Aq.	85·4	....	100·00	.....	100·00
Or:					Proust.
CuO	40·0	....	46·84	.....	40
Cl—O	27·4	....	32·08	.....	24
2HO	18·0	....	21·08	.....	36
	85·4	....	100·00	.....	100

The solution of protochloride of copper in a small quantity of water is emerald-green, but a large quantity turns it pale blue. The concentrated solution assumes a yellow colour on the addition of strong hydrochloric acid. With oil of vitriol it solidifies into a brown mass. Characters traced on paper with the solution turn yellow when heated.

Protochloride of copper is likewise soluble in alcohol and ether.

E. Cupric Oxychloride.—*a.* CuCl,2CuO.—An aqueous solution of protochloride of copper is precipitated with a quantity of potash not sufficient to decompose the whole of it, and the pale green precipitate—which is the hydrated compound—is washed and dried, and then heated till the water is driven off, whereby it is converted, first into a brown, and then into a black powder. (Kane, *Ann. Chim. Phys.* 72, 277.)

					Kane.
3Cu	96·0	....	65·13	.....	63·78
Cl	35·4	....	24·01	.....	23·59
2O	16·0	....	10·86	.....	10·77
CuCl,2CuO	147·4	....	100·00	.....	98·14

α. Mono-hydrated.— CuCl,2CuO + Aq.— Remains in the form of a chocolate-coloured powder, when the ter-hydrated compound *β* is kept for some time at a temperature of 138°.—*β. Ter-hydrated.*—CuCl,2CuO + 3Aq.—The anhydrous compound, when moistened with water, becomes very hot, and assumes a fine green colour, brighter than Brunswick-green. —The ter-hydrated compound heated to 138°, gives off 11·08 per cent. of water, and is converted into *α*, and at 260°, it gives 16·83 p. c., and is converted into the anhydrous compound.—*γ. Tetra-hydrated.*—The pale green precipitate above mentioned. Of a paler colour than Brunswick-green. Gives off 21·51 per cent. of water on ignition, and if afterwards moistened and dried at 38°, again takes up 16·78 per cent. (Kane.)

	At.			*α.*			Kane.
CuCl,2CuO	1	....	147·4	....	94·24	.....	93·55
HO	1	....	9·0	....	5·76	.....	6·45
			156·4	....	100·00	.....	100·00
	At.			*β.*			Kane.
CuCl,2CuO	1	....	147·4	....	84·52	.....	83·17
HO	3	....	27·0	....	15·48	.....	16·83
			174·4	....	100·00	.....	100·00

b. CuCl, 3CuO.—Obtained by gently heating the hydrated compound. Brown. Gives off oxygen at a red heat, and is converted into a compound of protoxide and dichloride of copper. (Proust.)

$$CuCl,3CuO = Cu^2Cl,2CuO + O.$$

c. CuCl, 4CuO.—Remains in the hydrated state, and in the form of a green powder, when NH^3,CuCl is treated with water. When heated, it gives off its water, and becomes chocolate-brown, and if afterwards exposed to the air, regains a portion of the water which it has lost. (Kane.)

Anhydrous.			*Hydrated.*			Kane.
5Cu	160·0	70·36	5Cu	160·0	56·86	56·31
Cl	35·4	15·57	Cl	35·4	12·58	
4O	32·0	14·07	4O	32·0	11·37	
			6HO	54·0	19·19	19·32
CuCl, 4CuO	227·4	100·00	+ 6Aq	281·4	100·00	

F. Hypochlorite of Cupric Oxide, or Cupric Hypochlorite.—This salt cannot be obtained by precipitating blue vitriol with hypochlorite of lime, inasmuch as a reaction is thereby produced similar to that with zinc (p. 31). — It is formed by dissolving cupric oxide in aqueous hypochlorous acid. The solution, when distilled, gives off hypochlorous acid and probably also free oxygen, and leaves a fine green oxychloride, which, when treated with excess of cupric oxide, gives off oxygen and chlorine, and is converted into an insoluble oxychloride. (Balard.)—Cupric oxide dissolves readily in chlorine water (Chenevix); the saturated solution contains an equal number of atoms of cupric oxide and chlorine [CuCl + CuO,ClO], and decolorizes indigo after half an hour's boiling; when distilled, it leaves hypochlorous acid. (Balard.)

G. Chlorate of Cupric Oxide, or Cupric Chlorate.—Aqueous chloric acid readily dissolves cupric oxide, forming a greenish-blue solution, which yields green crystals having a slightly acid reaction; they produce a green flame when thrown on glowing coals, and deliquesce in the air. (Vauquelin.)—¶ According to Wächter (*Ann. Pharm.* 52, 233), chlorate of cupric oxide is composed of CuO, ClO^5 + 6 Aq., and crystallizes in octohedrons, which are deliquescent and soluble in alcohol. At 100° it is decomposed, giving off a few gas-bubbles, and leaving a green substance which suffers further decomposition at 260°, and is insoluble in water, but soluble in acids. This substance appears to be a basic chlorate, inasmuch as its solution in nitric acid gives no precipitate with a silver-salt ¶.

H. Perchlorate of Cupric Oxide, or Cupric Perchlorate.—The solution of cupric oxide in aqueous perchloric acid, evaporated in the hot-air chamber, yields large, blue, deliquescent crystals which redden litmus. Paper saturated with the solution and then dried, deflagrates when thrown on red-hot coals, producing vivid sparkling, a blue light, and a green flame. Soluble in alcohol. (Serullas, *Ann. Chim. Phys.* 46, 306.)

Copper and Fluorine.

A. Difluoride of Copper, or Cuprous Fluoride. — Hydrated cuprous oxide treated with excess of aqueous hydrofluoric acid, is immediately converted into red cuprous fluoride, which must be collected on a filter, quickly washed with alcohol, and then pressed and dried.—Red; fuses when heated, appearing black while in the liquid state, but resuming its scarlet colour on cooling.—In the dry state, it is permanent in the air,

but when moist, it is converted first into a yellow mixture of cupric fluoride and hydrated cuprous oxide:

$$2Cu^2F + O = 2CuF + Cu^2O,$$

and afterwards into green cupric oxyfluoride:

$$2CuF + Cu^2O + O = 2(CuF + CuO).$$

Insoluble both in water and in excess of hydrofluoric acid, but soluble in strong hydrochloric acid. In the latter it forms a black solution, from which it is precipitated by water in the form of a powder, which is white at first but afterwards becomes rose-coloured. (Berzelius, *Pogg.* 1, 28.)

B. Protofluoride of Copper, and Monobasic Hydrofluate of Cupric Oxide.—Formed by dissolving cupric oxide or its carbonate in excess of aqueous hydrofluoric acid (metallic copper is not sensibly dissolved by the acid) and evaporating the resulting blue solution. As the excess of acid goes off, small, light blue crystals separate from the liquid. (Scheele; Gay-Lussac & Thénard; Berzelius.) If the quantity of cupric carbonate is sufficient to neutralize the greater part of the acid, the compound separates out during the digestion; with a still larger quantity of carbonate, the basic compound C is formed. (Berzelius.) The crystals, which are but sparingly soluble in cold water, are decomposed by hot water, yielding an acid solution and the insoluble basic compound C. The crystals heated with oil of vitriol, yield 116 per cent. of cupric sulphate, and, when ignited with excess of lead-oxide, give off 26·3 per cent. of water. (Berzelius.)—Protofluoride of copper combines with the fluorides of the alkali-metals, forming black compounds. (Berzelius; *comp.* Unverdorben, *N. Tr.* 9, 1, 34.)

	Crystallized.				Berzelius.
Cu	32·0	....	46·58		
F	18·7	....	27·22		
2HO	18·0	....	26·20	.....	26·3
CuF,2HO	68·7	....	100·00		
Or:					Berzelius.
CuO	40·0	....	58·23	.....	58
HF	19·7	....	28·67		
HO	9·0	....	13·10		
CuO,HF + Aq.	68·7	....	100·00		

C. Hydrated Cupric Oxyfluoride, or Bibasic Hydrofluate of Cupric Oxide.—1. Formed by digesting aqueous hydrofluoric acid with excess of cupric carbonate.—2. By decomposing B with boiling water.—Pale green powder insoluble in water. (Berzelius.)

					Berzelius.	Or:			
CuF	50·7	....	50·85	....		2CuO	80·0	....	80·24
CuO	40·0	....	40·12	....		HF	19·7	....	19·76
HO	9·0	....	9·03	....	9·3				
CuF,CuO + Aq.	99·7	....	100·00				99·7	....	100·00

D. Borofluoride of Copper. — CuF,BF^3. — By precipitating the baryta-salt with blue vitriol. The filtrate, when evaporated to the consistence of a syrup, solidifies on cooling, and forms a blue mass of needles which quickly become moist on exposure to the air. (Berzelius.)

Copper and Nitrogen.

A. Nitride of Copper.—*a. With very great excess of Copper.*—Copper wire ignited in a porcelain tube through which a stream of ammoniacal gas is passed, neither increases nor diminishes in weight, but becomes very brittle and yellow or yellowish-white. (Thénard.) It increases from $\frac{1}{300}$ to $\frac{1}{275}$ in absolute weight, and its density decreases in the former case to 8·866, in the latter to 7·792. When the brittle copper thus obtained is fused in a retort, it gives off no gas, but a yellowish-brown substance makes its appearance between it and the retort. (Savart, *Ann. Chim. Phys.* 37, 326.)—The specific gravity of the copper sinks to 5·5; and the metal becomes more laminar and more porous, acquires a crystalline aspect, and assumes various tints of grey, yellow, greenish, orange, rose-red or purple-red. Nevertheless it contains but little foreign matter; but it probably takes up, during the process, a large quantity of nitrogen, which it afterwards gives off, so that the particles of the copper are left with considerable intervals between them. (Despretz, *Ann. Chim. Phys.* 42, 122.)—When dry ammoniacal gas is passed over red-hot copper wire, and then through water to absorb that which remains undecomposed, the remaining gaseous mixture is found to contain in 100 parts, not 75 vol. hydrogen and 25 vol. nitrogen, as should be produced by the decomposition of ammoniacal gas, but 86 vol. hydrogen to 14 vol. nitrogen; consequently part of the nitrogen must have been taken up by the copper. (Pfaff, *Pogg.* 42, 164.)—When dry ammoniacal gas is passed over finely divided copper (reduced from the protoxide by hydrogen at the lowest temperature possible) heated just to the point at which decomposition takes place, the resulting gaseous mixture contains 14·1 pts. nitrogen to 3 pts. hydrogen (no deficiency of nitrogen, therefore, but rather an excess, amounting to 0·1 pt. and probably arising from admixed air). Copper fused in ammoniacal gas retains its properties even for a considerable time. (Schrötter, *Ann. Pharm.* 37, 131; *comp.* Kastner, *Kastn. Arch.* 12, 455.)

b. Somewhat richer in Nitrogen?—By a process similar to that adopted in the preparation of nitride of zinc (p. 33), the sal-ammoniac being kept constantly in excess to prevent the deposition of metallic copper—a blue colour is produced in the liquid, and nitride of copper collects at the negative pole in the form of a chocolate-coloured aggregation, which, when washed and dried, exhibits a density of 5·9. Ten grains of this substance give off 0 214 cub. in. nitrogen gas when heated, and leave a residue of red metallic copper. (Grove, *Phil. Mag. J.* 19, 100; also *Pogg.* 54, 101.)

c. Cu^6N.—When protoxide of copper (obtained by precipitating blue vitriol at a boiling heat with caustic potash) is heated to 250° in a glass tube immersed in a bath of linseed oil, and subjected to the action of dry ammoniacal gas, it is converted into a green powder, with rise of temperature, evolution of nitrogen gas, and formation of water. At too high a temperature, metallic copper is obtained instead of the green powder. Cupric oxide obtained by igniting the nitrate, requires a high temperature to convert it into nitride, and the product is mixed with a considerable quantity of undecomposed oxide. If the hydrate or carbonate of cupric oxide be used, the heat at first must not exceed 130°, but when the formation of water ceases, it may be raised to the boiling point of linseed oil. If the temperature be raised at once to 250°, the heat developed by the action of the ammonia increases it to such a point, that the nitride

and protoxide of copper are converted into a mixture of metallic copper and dioxide, with evolution of water, nitrogen gas, and nitric oxide.—The stream of gas having been kept up for 8 hours, and no more water being formed, the green powder is shaken up, again treated with ammoniacal gas for three hours, then again shaken up, once more exposed to ammoniacal gas, having meanwhile been triturated in a mortar, &c. To produce 20 grammes of nitride of copper, the passage of the gas must be continued for 120 hours. (Schrötter.)—To free the resulting green powder from adhering cuprous oxide, it must be repeatedly digested with a mixture of caustic ammonia and carbonate of ammonia, and afterwards washed and dried; the colour of the powder then changes from olive-green to dark grey. (Berzelius, *Jahresber.* 21, 88.)

Soft, greenish-black powder (Schrötter); dark grey (Berzelius).

				Schrötter.							
				a.		*b.*		*c.*		*d.*
6Cu	192	93·2		90·965		90·965		83·433		92·76
N	14	6·8		7·041		6·516		6·516		7·24
H				0·111	NH^3	0·636		0·636		
							CuO	9·415		
Cu^6N	206	100·0		98·117		98·117		100·000		100·00

a is the mean of several analyses; the deficiency must be regarded as oxygen which remained with the nitride of copper in the form of cupric oxide. The hydrogen was probably in the state of ammonia, which seems to adhere to the compound very tenaciously; for, when the nitride of copper is exposed to a temperature near its decomposing point, and carbonic acid gas afterwards passed over it, ammonia is still evolved from it.—*b* is therefore the analysis *a* with the hydrogen estimated as ammonia. (Schrötter.) If the deficiency (=1·883) be regarded as oxygen and estimated as protoxide of copper, we get the calculation *c*; and finally, if the ammonia and cupric oxide be disregarded as unessential, the remainder gives the per-centage composition of pure nitride of copper as in *d*. (Gm.)

The formation of the nitride of copper takes place as shown in the following equation:—

$$6CuO + 2NH^3 = Cu^6N + 6HO + N.$$

Hence, 240 pts. (6 At.) of cupric oxide should yield 206 pts. (1 At.) nitride of copper, 54 pts. (6 At.) water, and 14 pts. (1 At.) nitrogen. According to the mean of three experiments, 240 parts of cupric oxide yield 216·65 nitride of copper, 37·08 water, and 12·04 nitrogen gas. The difference between these and the theoretical numbers arises perhaps from part of the cupric oxide remaining undecomposed. (Schrötter.)

Nitride of copper heated in the air to about 300°, is resolved into nitrogen gas and metallic copper, the decomposition being attended with a bright red glow. In oxygen gas, the decomposition takes place at a lower temperature; in carbonic acid or nitrogen gas, a temperature above 300° is necessary. If the nitride of copper is contaminated with cupric oxide, the nitrogen evolved is mixed with nitric oxide. Percussion or friction does not produce decomposition. (Schrötter.) The nitride purified by ammonia, decomposes at a lower temperature and with slight explosion, whereby the greater part of the substance is projected out of the tube. (Berzelius.)—Nitride of copper becomes heated in chlorine gas,

with formation of protochloride of copper and evolution of nitrogen, and in hydrochloric acid gas, with formation of protochloride of copper and sal-ammoniac. [The hydrochloric acid gas may perhaps form dichloride of copper: $Cu^6N + 4HCl = 3Cu^2Cl + NH^4Cl$.] Nitric acid oxidizes nitride of copper with great violence; sulphuric acid rapidly liberates nitrogen gas from it, while metallic copper remains behind. Other non-oxidizing acids act in the same manner, but more slowly in proportion as they are more dilute. (Schrötter, *Ann. Pharm.* 37, 136.) Dilute acids liberate ammonia and form cuprous salts. (Berzelius.)

B. Nitrite of Cupric Oxide, or Cupric Nitrite.—By precipitating nitrite of lead-oxide with blue vitriol, and filtering, a green liquid is obtained, which oxidizes when exposed to the air, especially if it be heated, and is converted into cupric nitrate. (Berzelius.)

C. Nitrate of Cupric Oxide, or Cupric Nitrate.—*a. Terbasic.*—Formed by heating *b* to a certain temperature and removing the undecomposed portion by water. (Proust.)—2. By decomposing the aqueous solution of *b* with a small quantity of alkali, or of hydrated cupric oxide or cupric carbonate, or by boiling it with metallic copper.—Green powder. Reduced to black oxide by heat. In contact with red-hot charcoal, it gives off nitrous fumes; oil of vitriol poured upon it liberates nitric acid. When boiled with potash, it leaves black oxide of copper. (Proust.) Sustains the heat of melting lead almost without decomposition; at a higher temperature, it gives off nitric acid, hyponitric acid, oxygen gas, and water. The water may be expelled without decomposing the salt. (Graham, *Ann. Pharm.* 29, 13.)—Insoluble in water, easily soluble in acids.

	Calculation,	according to Graham.	Berzelius.	Proust.
$3CuO$	120	65·57	66·0	67
NO^5	54	29·51	18·9	16
HO	9	4·92	15·1	17
$3CuO, NO^5 + Aq.$	183	100·00	100·0	100

¶ According to Gladstone (*Chem. Soc. Mem.* 3, 480), the composition of this salt is $4CuO, NO^5 + 3Aq$. The same formula is assigned to it by Gerhardt. Kühn (*Arch. Pharm.* 2nd ser. 50, 283) has obtained the same result with the salt produced by partial precipitation of the neutral salt with ammonia. ¶

b. Monobasic.—Formed by dissolving metallic copper, cupric oxide, or its hydrate or carbonate, in nitric acid. The salt cannot exist with less than 3 atoms of water. Hence, on treating cupric oxide with the strongest nitric acid, and pouring off the excess, there remains a green powder chiefly consisting of terbasic salt, and therefore insoluble in water. But if the specific gravity of the acid does not exceed 1·42, nothing but the normal salt is produced.—The blue solution deposits the salt in blue crystals, which have a caustic metallic taste, and cauterize the skin. When formed at a moderately high temperature, they are prismatic and contain 3 atoms of water; but if produced at very low temperatures, they are tubular, and contain 6 atoms of water. The latter effloresce in vacuo over oil of vitriol, giving off half their water. (Graham, *Ann. Pharm.* 29, 13.) The tabular crystals fuse at 38°, giving off water and acid, and passing first into salt *a*, and afterwards into black oxide, the latter amounting to 27 per cent. (Proust.) A temperature

of 65° is sufficient to convert the monobasic into the terbasic salt. (Graham.)

$$3(CuO,NO^5+3Aq.) = 3CuO,NO^5+Aq.+2(NO^5,4Aq.)$$

The crystals detonate slightly on red-hot coals, more strongly with phosphorus under the hammer. (Brugnatelli.) When the powder of these crystals is wrapped up in tinfoil, it fuses and is decomposed, with a rise of temperature sometimes sufficient to cause emission of sparks. (Higgins, *Crell. Chem. J.* 1, 171.) Paper saturated with the solution and dried, takes fire much below a red heat. When the solution of this salt is mixed with nitrate of ammonia and evaporated, decomposition takes place at a certain degree of concentration, attended with violent detonation.—Dissolves readily in water, and deliquesces in the air; likewise soluble in moderately strong nitric acid; but, according to Mitscherlich (*Pogg.* 18, 159), it is precipitated from its concentrated aqueous solution in the form of a crystalline powder, by nitric acid of specific gravity 1·522.

Calculation, according to Graham.

Ter-hydrated.			*Sex-hydrated.*			Proust.
CuO	40	33·06	CuO	40	27·02	27
NO^5	54	44·63	NO^5	54	36·49	
3HO	27	22·31	6HO	54	36·49	
$CuO,NO^5+3Aq.$	121	100·00	+6Aq.	148	100·00	

D. Cuprous Oxide with Ammonia.—Formed by inclosing in a stoppered vessel (1) copper-filings with aqueous ammonia and atmospheric air; (2) copper-filings with the compound of cupric oxide and ammonia; (3) cuprous oxide or hydrated cupric oxide with aqueous ammonia.—Colourless liquid, which gradually turns blue on exposure to the air, the colour proceeding from top to bottom. (Bergmann, *Opusc.* 3, 389; Proust.)

E. Cupric Oxide with Ammonia.—Formed by exposing the preceding solution to the air; or by bringing copper-filings in contact with aqueous ammonia and a sufficient quantity of air; or cupric oxide, either anhydrous or hydrated, with aqueous ammonia. If all acids, even carbonic acid, be excluded, the ammonia, according to Berzelius, appears to dissolve scarcely a trace of the anhydrous oxide; but on adding a drop of the solution of an ammoniacal salt, the oxide is abundantly dissolved. (*Comp.* Wittstein, *Repert.* 57, 32.)—Dark azure-blue liquid. Phosphorus decolorizes it, by forming the compound of cuprous oxide and ammonia, and ultimately precipitates the copper in the metallic state; zinc and cobalt likewise precipitate the copper. Iron reduces the copper imperfectly; arsenic, tin, and cadmium reduce it sparingly, and lead exhibits but mere traces of reduction. (Fischer, *Pogg.* 8, 492.) Iron exerts no action on the pure solution, but slowly precipitates metallic copper from the solution mixed with sal-ammoniac, common salt, nitre, or sulphate of potash, nodules composed of copper and ferrous hydrate forming on its surface at isolated points, and extending till the liquid is decolorized. A large excess of ammonia prevents this precipitation, especially if the solution be mixed with nitrate or sulphate of potash. (Wetzlar, *Schw.* 50, 101.)—Sulphurous acid added to the solution of cupric oxide in ammonia, throws down nearly all the copper in the form of red-brown cuprous oxide, containing small portions of sulphurous acid [and ammonia ?]. (A. Vogel.) The liquid, when diluted with a large quantity of

water, deposits the cupric oxide in the form of hydrate. Potash—of which a larger quantity is required in proportion as the ammonia is in greater excess—likewise precipitates the cupric oxide, at least after a while, in the form of hydrate [containing potash?] the precipitation, according to Berzelius, being complete; on boiling the liquid, black oxide of copper is immediately precipitated.

When ammonia, not in excess, is added to cupric salts, the precipitate usually consists of a basic salt free from ammonia; Kane, however, on one occasion, by precipitating a solution of cupric chloride with ammonia, obtained a blue precipitate resembling hydrated cupric oxide, which was easy to wash, and did not lose ammonia during the washing. This precipitate underwent no change at 149°; but at a somewhat higher temperature, it was decomposed with a slight hissing noise, yielding nitrogen gas, ammonia, a large quantity of water, and a red mixture of copper and cuprous oxide. It was found to be free from chlorine.

					Kane.
$2NH^3$	34	....	16·35	....	15·70
3CuO	120	....	57·69	....	57·19
6HO	54	....	25·96	....	
$2NH^3,3CuO+6Aq.$	208	....	100·00		

F. Carbonate of Cupric Oxide and Ammonia.—*Cuprico-ammonic Carbonate.*—By dissolving copper-filings (with excess of air), anhydrous or hydrated cupric oxide, or cupric carbonate, in aqueous sesquicarbonate or bicarbonate of ammonia.—100 parts of bicarbonate of ammonia dissolved in 1440 parts of water, take up in the course of 24 hours, 2·38 parts of anhydrous cupric oxide, or 17·03 of the hydrate. (Bischof, *Schw.* 64, 72.)—The solution has an azure-blue colour, somewhat paler than that of cupric oxide in caustic ammonia. When heated, it gives off carbonate of ammonia, boiling up suddenly and violently, and depositing nearly all the copper in dingy bluish-green crusts which contain ammonia (Bucholz, *Beitr.* 1, 92); it first deposits dingy green carbonate, and then brown oxide. (Bischof.) The solution, when slowly evaporated, yields no crystals but a green crust. (Bucholz.) Potash boiled with it, throws down black oxide of copper. (H. Rose.)

G. *Boride of Nitrogen and Copper?*—By proceeding with boracic acid and copper in a manner similar to that described for the preparation of boride of nitrogen and potassium (III. 70), a substance is obtained which gives off ammonia when treated with hydrate of potash. (Balmain.)

H. Cupro-hyposulphate of Ammonia.—Formed by supersaturating a somewhat dilute solution of cupric hydrophosphate with ammonia till the precipitate disappears. This liquid soon yields azure-blue, rectangular tables, containing 2 At. ammonia, 1 At. cupric oxide, and 1 At. acid; they are permanent in the air, and dissolve but sparingly in water, especially if it be cold. (Heeren.)

I. Ammonio-sulphate of Cupric Oxide.—Anhydrous cupric sulphate rapidly absorbs 53·97 per cent. of dry ammoniacal gas, with great rise of temperature and tumefaction; the product is a blue powder. This compound fuses at a moderate red heat, a large quantity of ammonia being given off, a little water and sulphite of ammonia formed, and a brown mixture left behind consisting of cupric sulphate and metallic

copper. It dissolves completely in water, forming an azure-blue solution. (H. Rose, *Pogg.* 20, 150.)

			H. Rose.
$5NH^3$	85	34·70	35·05
$2CuO$	80	32·65	64·95
$2SO^3$	80	32·65	
$5NH^3+(2CuO,SO^3)$	245	100·00	100·00

K. Cupro-sulphate of Ammonia.—*Cuprum ammoniacale, Kupfersalmiak.*—Formed by supersaturating blue vitriol, either pounded or dissolved in a small quantity of water, with ammonia, till the precipitate is completely redissolved.—Crystallizes on evaporation—or better, on carefully covering the solution with alcohol, or exposing it a low temperature—in dark azure-blue, transparent crystals, having somewhat the form of *Fig.* 65, but very long and thin. When the ammoniacal solution is agitated with alcohol, the salt is precipitated in the form of a blue crystalline powder.—It must be quickly dried between bibulous paper, and kept in well-closed vessels:

	Crystallized.		Berzelius.	Brandes.
$2NH^3$	34	27·64	26·40	21·410
CuO	40	32·52	34·00	33·017
SO^3	40	32·52	32·25	31·753
HO	9	7·32	7·35	13·358
$NH^3,CuO+NH^4O,SO^3$	123	100·00	100·00	99·538

When exposed to the air, it gives off ammonia, first becoming light blue and opaque, and afterwards changing to a green powder, which, according to Kühn, is a mixture of sulphate of ammonia and quadrobasic sulphate of cupric oxide.—When heated for some time to a temperature not exceeding 149°, it gives off 1 atom of ammonia and 1 atom of water, and is converted into an apple-green powder, amounting to 98·4 p. c. of the original salt, and composed of NH^3,CuO,SO^3. The latter, when very gradually heated to 205°, still gives off ½ At. ammonia, leaving a residue of $NH^2,2CuO,SO^3$, and this, when gradually heated to 260°, gives off the last half atom of ammonia and leaves 65·1 per cent. of monosulphate of cupric oxide. Cuprosulphate of ammonia, when suddenly heated, gives off sulphate (sulphite: *Berzelius*) of ammonia as well as free ammonia, and leaves a residue of cuprous oxide, together with cupric sulphite. (Kane, *Ann. Chim. Phys.* 72, 265.)—Dissolves in 1½ pt. cold water. The aqueous solution, when exposed to the air, deposits quadrobasic sulphate of cupric oxide, which, if the liquid be warmed for some time in the air, partly redissolves, with evolution of ammonia, so that the liquid afterwards contains monobasic sulphate of cupric oxide together with sulphate of ammonia. (Kühn, *Schw.* 60, 343.) Quadrobasic sulphate of cupric oxide is likewise precipitated when the aqueous solution is largely diluted with water.—Zinc quickly precipitates metallic copper from the solution; cadmium and lead decompose it but slowly; arsenic decomposes it completely, with formation of cupric arsenite; bismuth, antimony, tin, and iron have no effect upon it. (Fischer, *Pogg.* 8, 492.)

L. Bibasic Sulphate of Cupric Oxide and Ammonia.—The residue left when cuprosulphate of ammonia is gradually heated to 149°. Apple-green powder. When exposed to the air, it gradually absorbs water and turns blue; if moistened with a small quantity, it becomes very hot and

changes to blue immediately; if it be then dried at 27°, one hundred parts of the powder will be found to have absorbed 27·8 parts (3 At.) of water. But an excess of water decomposes the powder into sulphate of ammonia, cuprosulphate of ammonia, and a precipitate of quadrobasic sulphate of cupric oxide. (Kane.)

$$5(NH^3,CuO,SO^3) = 3(NH^3,SO^3) + 2NH^3,CuO,SO^3 + 4CuO,SO^3.$$

	Anhydrous.				*Hydrated.*		
NH^3	17	...	17·52	NH^3	17	...	13·70
CuO	40	...	41·24	CuO	40	...	32·26
SO^3	40	...	41·24	SO^3	40	...	32·26
				3HO	27	...	21·78
NH^3,CuO,SO^3	97	...	100·00	+3Aq.	124	...	100·00

M. Sesquibasic Sulphate of Cupric Oxide and Ammonia.—$NH^3,2CuO,2SO^3$, or $NH^3,CuO,SO^3 + CuO,SO^3$.—The residue obtained by gently heating anhydrous cupric sulphate saturated with ammonia (Graham), or by gradually heating the cuprosulphate of ammonia to a temperature not above 205°. (Kane.)

N. Monobasic Sulphate of Cupric Oxide and Ammonia.—*Cuprico-ammonic Sulphate.*—Formed by mixing cupric sulphate with sulphate of ammonia, and leaving the solution to crystallize. A mixture of the concentrated solutions of sal-ammoniac and blue vitriol in equal volumes, likewise deposits crystals of the double sulphate, while the corresponding double chloride remains in solution. (A. Vogel.)—Light blue crystals easily soluble in water (Berzelius); of the form of sulphate of magnesia and ammonia. (Mitscherlich; *comp.* Miller, *Pogg.* 36, 477.) Sp. gr. 1·757. (Kopp.)—The crystals effloresce in warm dry air, fuse and turn green when heated, evolving water and sulphate of ammonia. They dissolve in 1½ times their weight of boiling water, and separate out for the most part as the liquid cools. (A. Vogel, *J. pr. Chem.* 2, 194.)

Crystallized.—Calculation, according to Berzelius.

NH^3	17	...	8·5
CuO	40	...	20·0
$2SO^3$	80	...	40·0
7HO	63	...	31·5
$NH^3,HO,SO^3 + CuO,SO^3 + 6Aq.$	200	...	100·0

O. Ammonio-diniodide of Copper.—1. One hundred parts of cuprous iodide absorb 19·728 parts of ammonia, the combination being attended with evolution of heat; but at a higher temperature, the whole of the ammonia is given off again. (Rammelsberg.)—2. Plates of copper are inclosed in a bottle, together with a cupric salt strongly supersaturated with ammonia—the liquid frequently shaken till it loses its colour—and then poured into a bottle containing aqueous iodide of potassium, which must be afterwards closed. The compound of cuprous oxide and ammonia then separates, partly in colourless, shining prisms, partly as a white, crystalline meal. Neither of these can be dried without decomposition, inasmuch as they turn green and give off ammonia when exposed to the air. The colourless liquid from which the compound has separated, turns blue in the air, from formation of the ammonia-compound of cupric iodide. (Levol, *N. J. Pharm.* 4, 328.)

niacal odour and deposits a green powder. Boiling water immediately produces the green powder. Acids added to the blue solution throw down cuprous iodide, while iodine remains in solution. Cold alcohol or ether exerts no action upon it; boiling alcohol becomes brown by acting on the compound, and gradually imparts a green colour to the residue. (Berthemot.)

The green flakes, when heated, give off much water and a little ammonia, then yield a sublimate of hydriodate of ammonia, and leave a brown-red residue containing cuprous iodide. (Rammelsberg.)

Q. Cupro-iodate of Ammonia.—The saturated solution of cupric iodate in hot aqueous ammonia yields azure-blue crystals on cooling; alcohol added to the mother-liquid throws down an additional quantity of the double salt, in the form of a crystalline powder. When heated, it gives off ammonia, iodine, oxygen gas, and water. With water it forms a blue liquid, a light blue powder being separated, which, even after long washing, still contains a considerable quantity of iodic acid. (Rammelsberg, *Pogg.* 44, 569.)

R. Ammonio-dibromide of Copper.—The solution of dibromide of copper in ammonia yields crystals. (Berthemot.)

S. Ammonio-protobromide of Copper.—*a.* $5NH^3,2CuBr$.—Anhydrous protobromide of copper introduced into ammoniacal gas becomes heated, swells up, and crumbles to a bulky blue powder. This compound, when heated, gives off ammonia and a small quantity of hydrobromate of ammonia, and leaves a mixture of protobromide and protoxide of copper. It dissolves completely in a small quantity of water, forming a deep blue solution; but this liquid, when diluted, becomes turbid and deposits hydrated cupric oxide, which turns black when the liquid is heated. (Rammelsberg.)

b. $3NH^3,2CuBr$.—Alcohol added to a concentrated solution of cupric bromide supersaturated with ammonia, throws down dark green crystals. These crystals, when treated with water or when heated, behave like the compound *a.* (Rammelsberg, *Pogg.* 55, 246.)

					Rammelsberg.
$5NH^3$	85·0		27·79		28·98
$2CuBr$	220·8		72·21		71·02
$5NH^3,2CuBr$	305·8		100·00		100·00

					Rammelsberg.
$3NH^3$	51·0		18·77		19·98
$2CuBr$	220·8		81·23	Cu	23·55
$3NH^3,2CuBr$	271·8		100·00		

T. Cupro-bromate of Ammonia.—Precipitated in the form of dark blue needles and a crystalline powder, on the addition of alcohol to a solution of cupric bromate in aqueous ammonia. When heated, it is decomposed, with a fiery explosion, yielding nitrogen gas, bromine, ammonia, and water, whereby the greater part of the oxide and bromide of copper is mechanically carried off. Turns green when exposed to the air. Dissolves completely in a small quantity of water, forming a blue *liquid;* and on adding a larger quantity of water, a bluish-green substance

is precipitated, which, after a little washing, exhibits the characters of pure hydrated cupric oxide; ammonia and bromate of ammonia remain dissolved in the water. (Rammelsberg, 52, 92.)

	Crystallized.			Rammelsberg.
$2NH^3$	34·0	17·67		16·66 to 17·35
CuO	40·0	20·79		22·84 ,, 22·07
BrO^5	118·4	61·54		
$NH^3,CuO + NH^3,BrO^5$	192·4	100·00		

U. Ammonio-dichloride of Copper.—Dichloride of copper forms a colourless solution with aqueous ammonia. Protosulphide of phosphorus forms therewith a red-brown precipitate (Berzelius), and potash throws down from it the hydrated dioxide, provided the ammonia is not in too great excess. (H. Rose.)

V. Dichloride of Copper and Ammonium.—*Cuproso-ammonic Chloride.*—The solution of cuprous chloride in strong hydrochloric acid, mixed with small quantities of ammonia, deposits transparent crystals, which appear to be cubes. (Gm.)—2. By the electrolytic method (I, 400, 401), the compound is obtained, sometimes in octohedrons, which are transparent and colourless at first but afterwards assume an amethyst-red tint—sometimes in six-sided prisms—sometimes in crystals of a different form, which are first colourless and afterwards yellow, and from which water extracts the sal-ammoniac. A similar compound is likewise formed when a solution of sal-ammoniac in which copper is immersed, is exposed to the air. (Becquerel.)

W. Ammonio-protochloride of Copper.—*a. With 3 At. Ammonia.* $3NH^3,CuCl$.—Protochloride of copper rapidly absorbs ammoniacal gas and swells up to a blue powder. (Faraday.) The absorption is very rapid at first, then becomes continually slower, and the whole quantity of ammonia absorbed amounts to 73·7 per cent. (H. Rose, *Pogg.* 20, 155.) The compound fuses when heated, and gives off its ammonia. (Faraday.) On the application of heat, it first turns green and gives off ammonia, and then fuses, yielding a sublimate of sal-ammoniac and a residue of dichloride of copper. (H. Rose.) At 149°, it gives off only 2 At. ammonia, so that the residue consists of $NH^3,CuCl$. (Kane.) The compound, when exposed to the air, turns green and gives off ammonia. (H. Rose.) It dissolves completely in water, forming a blue solution. (Faraday, H. Rose.)

				H. Rose.
$3NH^3$	51·0	43·07		42·43
CuCl	67·4	56·93		57·57
$3NH^3,CuCl$	118·4	100·00		100·00

Cadmium immersed in the blue solution of cupric chloride in excess of aqueous ammonia, reduces the copper completely, but throws down at the same time a small quantity of basic salt; iron reduces only a part of the copper; lead, a little; antimony, bismuth, and tin, none. (Fischer.) Protosulphide of phosphorus added to the solution throws down a black-brown precipitate. (Berzelius.)

b. With 2 At. Ammonia.—$2NH^3,CuCl + HO$, or $NH^3,CuO + NH^3,HCl$. When ammoniacal gas is passed through a hot saturated solution of cupric

chloride in water, till the precipitate which forms at first is completely redissolved, during which process the liquid is kept almost boiling by the heat developed by the absorption of the gas, the resulting solution yields, on cooling, small, dark blue octohedrons, and square prisms with four-sided summits. These crystals must be quickly dried between bibulous paper at the ordinary temperature of the air, and in a place where they will not be exposed to acid fumes; but even when that precaution is taken, they are very apt to turn green on the surface from loss of ammonia. At a temperature not above 149°, they give off all their water and half their ammonia, leaving 76·3 per cent. of the following compound, $NH^3,CuCl$, which undergoes further decomposition at a higher temperature. (Kane, *Ann. Chim. Phys.* 72, 273.)

	Crystallized.				Kane.
$2NH^3$	34·0	....	30·80	.....	28·83
Cu	32·0	....	28·98	.....	28·73
Cl	35·4	....	32·06	.....	32·19
HO	9·0	....	8·16		
$2NH^3,CuCl + Aq.$	110·4	....	100·00		

c. With 1 *At. Ammonia.*—$NH^3,CuCl$.—1. The residue left on heating *a* or *b* to 149°. (Kane.)—2. Formed by saturating chloride of copper at a high temperature with ammoniacal gas. (Graham.) Green powder. When heated somewhat strongly, it gives off nitrogen, ammonia, and sal-ammoniac, and leaves dichloride of copper:

$$6(NH^3,CuCl) = 3Cu^2Cl + 3(NH^3,HCl) + 2NH^3 + N.$$

It is decomposed by water, yielding sal-ammoniac and the compound *b*, which dissolve, together with a bluish-green residue of cupric oxychloride. CuCl,4CuO (p. 442). (Kane.)

$$6(NH^3,CuCl) + 4HO = 4(NH^3,HCl) + 2NH^3,CuCl + CuCl,4CuO.$$

NH^3	17·0	.....	20·14
CuCl	67·4	.....	79·86
$NH^3,CuCl$	84·4	.....	100·00

The anhydrous compound, CuCl,2CuO absorbs from 10·4 to 11·1 per cent. of ammonia, becoming slightly heated, but retaining its brown colour: it is thereby converted into $NH^3 + CuCl,2CuO$. (Kane.)

X. Protochloride of Copper and Ammonium. — *Cuprico-ammonic Chloride.* *a.* $NH^4Cl,CuCl + 2Aq.$—1. Formed by mixing the concentrated aqueous solutions of equal equivalents of sal-ammoniac and protochloride of copper, and cooling the mixture to the crystallizing point. 53·4 parts of sal-ammoniac and 67·4 pts. anhydrous chloride of copper, or 85·4 pts. of the crystallized chloride, is the proportion required. (Mitscherlich, *J. pr. Chem.* 19, 449; Graham, *Ann. Pharm.* 29, 32.)—2. Concentrated solutions of blue vitriol and sal-ammoniac, mixed in equal volumes and then evaporated and cooled, first yield crystals of the double sulphate and afterwards of the double chloride. (A. Vogel, *J. pr. Chem.* 2, 194.)—3. Aqueous protochloride of copper is supersaturated with ammonia, and the filtered liquid concentrated by evaporation and slowly cooled to the crystallizing point. (Cap & O. Henry, *J. Pharm.* 23, 617; also *J. pr. Chem.* 13, 184.) The solution acquires a bluish-green colour during the evaporation, and deposits

bluish flakes. (Kane.) As the excess of ammonia is driven off by evaporation, protochloride of copper and ammonium, together with the ammonia-compound of cupric oxide, appears to form in the solution; and the latter seems to be, for the most part, decomposed by the heat into ammonia which escapes, and a basic salt which is precipitated :

$$2CuCl + 2NH^3 + HO = (NH^3, HCl, CuCl) + NH^3, CuO.$$

Cupric oxide, either anhydrous or anhydrated, and likewise the carbonate, dissolve with facility in aqueous sal-ammoniac, forming a blue solution (Brett), which gives off ammonia on boiling (L. Thompson); in this case also the same compound is probably formed.

Square-based octohedrons. (Mitscherlich.) Blue or sometimes greenish-blue octohedrons, which yield a light blue powder, and have a disagreeable coppery taste. (Cap & Henry.) Siskin-green crystals, permanent in the air. (A. Vogel.)

	Crystallized.				Cap & Henry.
NH^3	17·0	....	12·25	.....	14·46
Cu	32·0	....	23·05	.....	25·03
Cl	35·4	....	25·50	.....	27·57
HCl	36·4	....	26·23	.....	26·34
2HO	18·0	....	12·97	.....	6·60
$NH^3, HCl + CuCl + 2Aq$	138·8	....	100·00	.....	100·00

The calculation is made according to the statements of Graham and Mitscherlich, which agree; the analysis by Cap & Henry corresponds to the formula, $NH^3, HCl + CuCl + Aq$.

The salt retains its 2 atoms of water with great tenacity, and cannot be completely dried without volatilization of sal-ammoniac. (Graham.) When heated, it gives off water and turns greenish, but recovers its blue colour on being moistened with water. At a higher temperature, it fuses, gives off acid vapours, accompanied by sal-ammoniac and a small quantity of chloride of copper, and solidifies in a radiated mass on cooling. (Cap & Henry.) It is less soluble in water than the protochloride of copper. (Graham.) It dissolves in water with partial decomposition and separation of a green powder, while the solution is acid and greenish. In alcohol, especially when hot, it dissolves completely and without decomposition. (Cap & Henry.) The aqueous mixture of protochloride of copper and sal-ammoniac is green, but acquires a transient yellow colour when heated, as do likewise characters traced on paper with it.

¶ *b.* $NH^4Cl, 2CuCl + 4Aq$.—By saturating one part of hydrochloric acid with ammonia, 2 pts. of the same acid with cupric carbonate, and mixing the solutions, this salt is obtained in fine bluish-green crystals, isomorphous with the corresponding nickel and cobalt-compounds, and soluble in 2 parts of water.

					Hautz.
NH^4	18·0	....	8·03	.....	8·08
2Cu	64·0	....	28·55	.....	27·79
3Cl	106·2	....	47·37	.....	47·39
4HO	36·0	....	16·05	.....	16·46
$NH^4Cl, 2CuCl + 4Aq$.	224·2	....	100·00	.....	99·72

(Hautz, *Ann. Pharm.* 66, 281.) ¶

Y. Cupro-nitrate of Ammonia.—1. Formed by saturating cupric nitrate with ammonia. (Newmann.)—2. By passing ammoniacal gas

through a hot saturated solution of cupric nitrate, till the precipitate redissolves, and leaving the solution to crystallize by cooling. (Kane.)—3. When a basin containing aqueous ammonia, and another containing a concentrated solution of cupric nitrate, are placed together under a bell-jar, a crystalline powder forms in the latter, which, by recrystallization in hot water, may be obtained in distinct crystals. (Berthier.)—Blue crystals (Newmann), needles intersecting each other (Kane).—Gives off traces of ammonia when heated, but no water if it has been previously well dried. The mass exhibits small specks of black oxide of copper, fuses, and at a higher temperature explodes with a violent hissing noise, forming a cloud of gaseous matter, and leaving a residue of cupric oxide. (Kane.) According to Berzelius, also, the salt exhibits hissing, but not detonating explosion; according to Newmann, it leaves, when dissolved in alcohol and evaporated to dryness, a residue which detonates like fulminating gold when heated. It dissolves easily in water; a small quantity of acid throws down trinitrate of cupric oxide.

	Crystallized.				Kane.
$2NH^3$	34	....	26·56	.....	25·23
CuO	40	....	31·25	.....	31·03
NO^5	54	....	42·19		
	128	....	100·00		

$NH^3,CuO+NH^3,NO^5$; or, according to Kane, Cu,NH^2+NH^3,HO,NO^5, *i. e.* a compound nitrate of ammonia with amide of copper.

¶ Z. Azophosphate of Cupric Oxide.—When cupric sulphate is added to a slightly acid aqueous solution of chlorophosphide of nitrogen decomposed by ammonia and alcohol, and the mixture boiled, a pale blue flocculent copper-salt precipitates. This compound, when heated, swells up, becomes black and afterwards lighter in colour, and evolves ammonia, vapour of water, and the white sublimate already mentioned (p. 259), as produced by the decomposition of the corresponding ferric-salt. It is wholly decomposed by a cold solution of potash.

					Gladstone.
$3CuO$	120	....	42·41	.....	42·42
$2P$	64	....	22·62	.....	
N	14	....	4·94	.....	4·72
$2H$	5	....	1·76	.....	1·94
$10O$	80	....	28·27	.....	
$3CuO,P^2NO^5+5Aq.$	283	....	100·00		

(Gladstone, *Chem. Soc. Qu. J.* 3, 147.) ¶

Copper and Potassium.

A. Alloy of Copper and Potassium.—According to Serullas, copper heated to redness with cream of tartar does not become alloyed with potassium. According to Karsten, copper thus treated takes up a quantity of potassium not exceeding 0·13 per cent., and is thereby rendered somewhat less ductile when hot.

B. Cuprous Oxide with Potash.—*a*. Hydrate of potash fused in a copper crucible out of contact of air, forms a red mass, from which water

separates the greater part of the dioxide in the form of a brick-red powder; a small portion, however, goes into the potash solution. — *b.* When cuprous oxide, either anhydrous or hydrated, is treated with excess of caustic potash, a small quantity dissolves. The colourless liquid turns brown with sulphuretted hydrogen and deposits sulphide of copper. (Chodnew, *J. pr. Chem.* 28, 217.)

B. Cupric Oxide with Potash.—*a.* Hydrate of potash fuses with cupric oxide to a green, transparent liquid; water withdraws the potash from this mass, and leaves the cupric oxide undissolved. (Berzelius.) One part of cupric oxide heated to commencing redness, dissolves completely in 4 or 6 parts of pure hydrate of potash (*Potasse à l'alcohol*). When the cooled mass is treated with water, oxygen gas escapes, in consequence of the previous formation of peroxide of potassium, while flakes and crystals of cupric oxide free from potash remain undissolved. The crystals are formed during the solidification of the mass, for they may be recognized before the action of the water; they separate during the process of solidification from their solution in peroxide of potassium (or rather in hydrate of potash: Berzelius); the flakes are that portion of the cupric oxide which remain in combination with the potash-hydrate even when the mass is solidified. When common-hydrate of potash containing lime is used, scarcely a trace of crystals is produced. Cupric oxide ignited for some time with hydrate of potash, is converted into cuprous oxide, and on treating the mass with water, the latter is obtained in smaller red crystals. (Becquerel, *Ann. Chim. Phys.* 51, 122; also *Schw.* 66, 401.)—The compound of cupric oxide and potash is obtained on fusing hydrate of potash in a copper crucible, or cuprous oxide and hydrate of potash in a silver crucible, the air having access to the mass. The compound is dark blue, somewhat green on the surface. The longer the fusion is continued, the greater is the quantity of cupric oxide dissolved; the proportion, however, does not exceed 1 part in 173 to 200 of potash-hydrate. The oxide is not completely separated on treating the mass with water; a portion passes into the solution, and imparts a blue colour to it. (Chodnew, *J. pr. Chem.* 28, 217.)

b. Strong potash-ley mixed in excess with hydrated cupric oxide or any salt of copper, dissolves a portion of the oxide. The blue solution, when heated for some time, deposits black oxide of copper, and on addition of water, the blue hydrate. (Proust, A. Gehl. 6, 561;—*comp.* Roloff, *A. Gehl.* 6, 440.)—The blue solution is obtained either by treating the fused compound *a* with water, or by dropping a dilute solution of copper into an excess of strong, cold solution of potash, which redissolves the precipitate first formed. (If the liquids are hot, a separation of black cupric oxide takes place.) In this combination, 38·5 parts of potash-hydrate are required for 1 part of dissolved cupric oxide. The solution when once obtained is not rendered turbid either by boiling or by the addition of water (contrary to Proust's statement), but is rather made clearer by boiling; even the ignited oxide dissolves in caustic potash after continued boiling, the solution taking place the more easily as the potash-ley is stronger. (Chodnew.) Berzelius suspects that the power possessed by the potash to dissolve the cupric oxide may have arisen from the presence of organic matter.

c. Potash added to the solution of cupric oxide in ammonia, or to carbonate of cupric oxide and ammonia, throws down light-blue flakes of hydrated cupric oxide containing potash, from which warm water extracts

the whole of the potash. (Berzelius.)—Grouvelle (*Ann. Chim. Phys.* 17, 356) states that hydrated cupric oxide precipitated from copper-salts by excess of potash, contains potash in a state of such intimate combination, that it cannot be extracted by water, and is even retained in the anhydrous oxide which is formed on boiling the hydrate with water; it may, however, be detected by evaporation to dryness, and ignition with nitric acid.

According to a former statement of Berzelius (*Schw.* 30, 16...9), cupric oxide in excess, ignited with carbonate of potash, drives out $\frac{1}{4}$ of the carbonic acid, so that $KO,CuO+3KO,CO^2$ is produced; water added to the mass dissolves out the 1 atom of potash and the 3 atoms of the carbonate of potash, and leaves cupric oxide.—According to Fellenberg (*Pogg.* 44, 447), carbonate of potash ignited with cupric oxide does not give off a trace of carbonic acid. Berzelius (*Jahresber.* 19, 247) arrived at the same result, and attributes the evolution of carbonic acid which he observed in his former experiments, to the fact of his having used a porcelain retort, the silica of which expelled the carbonic acid from the carbonate of potash.—More recently Chodnew (*J. pr. Chem.* 28, 217) has found that carbonic acid is certainly evolved in this reaction, provided the heat be strong enough; and according to Dumas & Piria (*J. pr. Chem.* 27, 332), 1 atom of carbonic acid is expelled from 4 atoms of carbonate of potash,—a result agreeing perfectly with the former statement of Berzelius, according to which the quantity of carbonic acid driven off does not amount to the half. The subject requires further examination.

D. Carbonate of Cupric Oxide and Potash.—*Cuprico-potassic Carbonate.*—Aqueous carbonate of potash dissolves carbonate of cupric oxide, forming a pale blue solution (Hausmann, *Scher. J.* 4, 579); from the solution in bicarbonate of potash the double salt crystallizes in octohedrons. (*Schw.* 9, 9.) Iron immersed in this solution does not precipitate the copper, unless sal-ammoniac, common salt, nitre, or sulphate of potash is present. (Wetzlar, *Schw.* 50, 103.)

E Sulphide of Copper and Potassium.—*a.* 5 parts of ignited blue vitriol, heated to whiteness in a charcoal crucible with 5 parts of sulphate of potash, yield 5·6 parts of a metallic sulphide, which is tumefied and black, has an acrid and sulphurous taste, effloresces in the air, and gives up its sulphide of potassium to water, while sulphide of copper remains in the form of a black powder. (Berthier, *Ann. Chim. Phys.* 22, 294.)—*b.* 1 part of liver of sulphur ignited with 6 parts of copper-filings, yields a black, semi-fused mass, from which water extracts nothing but sulphate of potash. (Vauquelin, *Ann. Chim. Phys.* 6, 25.)—*c.* A copper vessel in which potash-ley is boiled with sulphur, becomes rapidly corroded. (*Paschenb.* 1781, 28.)—*d.* Becquerel, by the electrolytic method (I. 401), obtained silky needles of [hydrated ?] sulphide of copper and potassium.

Protosulphide of copper is soluble in aqueous carbonate of potash. (Berzelius.)

F. Hyposulphite of Cuprous Oxide and Potash. — *Cuproso-potassic Hyposulphite.—a. With* 1 *At. Potash-salt.*—Aqueous hyposulphite of potash forms with sulphate or acetate of cupric oxide, a green mixture, from which, after a while, the double salt is precipitated in the form of a crystalline powder. (Rammelsberg.)—The reduction of the cupric to cuprous oxide which here takes place, is accompanied by the

formation, not of sulphuric, but probably of tetrathionic acid. (Fordos & Gélis, *N. J. Pharm.* 4, 338.) [Perhaps according to the following formula] :

$$4(KO,S^2O^2) + 2(CuO,SO^3) = 2(KO,SO^3 + KO,Cu^2O,2S^2O^2) + KO,S^4O^5.$$

(Compare, on the other side, Lenz, under the head of *Hyposulphite of Cupric Oxide and Soda.*)—The salt quickly turns brown while being dried in the air. It blackens when heated, whereupon water extracts from it sulphate of potash free from sulphide of potassium. When boiled with water, it disintegrates and yields black sulphide of copper, the water taking up sulphurous and sulphuric, but no hyposulphurous acid :

$$KO,Cu^2O,2S^2O^2 = 2CuS + KO,SO^3 + SO^2.$$

With heated potash it is resolved into yellow hydrated cuprous oxide and hyposulphite of potash. It dissolves with difficulty in water. (Rammelsberg, *Pogg.* 56, 321.)

	Crystallized.				Rammelsberg.
KO	47·2	....	20·24	.....	17·86
Cu^2O	72·0	....	30·87	.....	31·40
$2S^2O^2$	96·0	....	41·17	.....	42·07
2HO	18·0	....	7·72	.....	8·67
$KO,S^2O^2 + Cu^2O,S^2O^2 + 2Aq.$	233·2	....	100·00	.....	100·00

b. With 3 At. Potash-salt.—Precipitated on the addition of alcohol to the saturated solution of the salt *a* in aqueous hyposulphite of potash, in the form of a heavy oil, which soon solidifies to a white mass. Dissolves more easily in water than *a*; the solution remains undecomposed on boiling, but hydrochloric acid liberates sulphurous acid from it, precipitating sulphur and afterwards sulphide of copper. Chloride of barium added to the solution, throws down white flakes of the barytic double salt, soluble in hydrochloric acid. Excess of ammonia forms a colourless liquid which turns blue in the air. (Rammelsberg.)

					Rammelsberg.
3KO	141·6	....	32·73	.....	31·24
Cu^2O	72·0	....	16·64	.....	15·41
$4S^2O^2$	192·0	....	44·39	.....	46·10
3HO	27·0	....	6·24	.....	7·25
$2(KO,S^2O^2) + Cu^2O,S^2O^2 + 3Aq.$	432·6	....	100·00	.....	100·00

G. Sulphite of Cuprous Oxide and Potash.—*Cuproso-potassic Sulphite.*—When solutions of cupric nitrate and sulphite of potash, not too dilute, are mixed in the cold, a yellow precipitate is formed, containing 85·2 sulphite of cuprous oxide and 14·8 sulphite of potash, which latter may be extracted by boiling water. The salt is insoluble in water.

H. Sulphate of Cupric Oxide and Potash.—*Cuprico-potassic Sulphate.*—Formed by dissolving pure or carbonated cupric oxide in aqueous bisulphate of potash, or by mixing monosulphate of potash with monosulphate of cupric oxide, and leaving the solution to crystallize. (F. C. Vogel, *Schw.* 7, 40.) By heating the crystals, the dry salt is obtained in the form of a green, friable mass, which fuses at a red heat, giving off a portion of its acid. (F. C. Vogel.) When cooled after fusion, it solidifies in a blue mass, which soon falls to pieces in scales or powder, with decrepitation and formation of cracks. (Graham, *Phil. Mag. J.* 4, 418; Böttger, *Pogg.* 50, 43.)

From the aqueous solution, the salt separates in combination with 6 atoms of crystallization-water, forming pale blue crystals, isomorphous with those of sulphate of magnesia and ammonia (Mitscherlich), and of specific gravity 2·137. (Kopp.) *Fig.* 84, $i : u'$ or $u = 104° 30'$; $i : a = 154° 20'$; $i : f = 116° 20$; $u' : u = 107° 35'$; $u : t = 126° 12'$. (Brooke, *Ann. Phil.* 23, 118.)—The crystals heated to 100° in the air, give off 11·27 p.c. (2 At.) of water. (Graham.) They are easily soluble in water. (F. C. Vogel.)

		Anhydrous.	
KO	47·2	.....	28·23
CuO	40·0	.....	23·92
$2SO^3$	80·0	.....	47·85
$KO,SO^3 + CuO,SO^3$	167·2	.....	100·00

	Crystallized.			F. C. Vogel.		Graham.
KO	47·2	....	21·34	.....	21·42	....	} 75·61
CuO	40·0	....	18·08	.....	18·00	....	
$2SO^3$	80·0	....	36·16	.....	36·08		
6HO	54·0	....	24·42	.....	24·50	....	24·39
$KO,SO^3 + CuO,SO^3 + 6Aq.$	221·2	....	100·00	.....	100·00	....	100·00

The aqueous solution when boiled, deposits a light green crystalline powder, consisting of a *basic double salt*, so that the liquid filtered from this deposit not only yields crystals of the normal salt, but ultimately a mother-liquid containing bisulphate of potash. The basic crystalline powder appears by analysis to consist of $KO,4CuO,4SO^3 + 4Aq$; different samples of it, however, gave different results, so that it must be regarded as a variable mixture of two basic salts. When boiled for some time with water, it leaves basic sulphate of cupric oxide, the water taking up the sulphate of potash, together with a small quantity of cupric oxide. (Brunner, *Pogg.* 15, 476; 32, 221.) Graham likewise obtained the basic double salt on boiling the solution, and found that it was decomposed during washing.

I. Seleniate of Cupric Oxide and Potash.—Exhibits characters similar to those of the sulphate. (Mitscherlich.)

K. Diniodide of Copper and Potassium.—*Cuproso-potassic Iodide.*—Becquerel obtained this salt in white needles by the electrolytic method. (I. 401.)

L. Dichloride of Copper and Potassium. — *Cuproso-potassic Chloride.*—Formed by boiling dichloride of copper in a small quantity of water, adding chloride of potassium till all the dichloride of copper is dissolved, and cooling the solution to the crystallizing point.—Anhydrous regular octohedrons $= 2KCl, Cu^2Cl$. (Mitscherlich, *Ann. Chim. Phys.* 73, 384.)—Becquerel, by the electrolytic method, obtained the same or a similar compound crystallized in tetrahedrons. (I, 401.)

M. Protochloride of Copper and Potassium. — *Cuprico-potassic Chloride.*—Formed by cooling a concentrated aqueous mixture of protochloride of copper and chloride of potassium. Square-based octohedrons $= KCl, CuCl + 2Aq$. (Mitscherlich.) Double six-sided pyramids. (Jacquelain.) Soluble in water and alcohol. (Berzelius, *Pogg.* 13, 458; *comp.* Boullay, *J. Pharm.* 12, 639; Graham, *Ann. Pharm.* 29, 32.)

	Anhydrous.				*Crystallized.*			Jacquelain.
K	39·2	....	27·61	K	39·2	....	24·50	.... 24·50
Cu	32·0	....	22·53	Cu	32·0	....	20·00	.... 19·81
2Cl	70·8	....	49·86	2Cl	70·8	....	44·25	.... 43·87
				2HO	18·0	....	11·25	.... 11·82
KCl, CuCl	142·0	....	100·00	+ 2Aq.	160·0	....	100·00	.... 100·00

N. Fluoride of Copper and Potassium.—KF, CuF.—Pale bluish-green, granular crystals, easily soluble in water. (Berzelius.)

Copper and Sodium.

A. Cupric Oxide with Soda.—*a.* Hydrate of soda likewise dissolves cupric oxide when fused with it. (Berzelius.) Cupric oxide is also slightly soluble in aqueous solution of soda.

B. Carbonate of Cupric Oxide and Soda.—*a.* Aqueous carbonate of soda, the bicarbonate more especially, dissolves a small quantity of cupric oxide, forming a pale blue solution.

b. Carbonate of soda heated with cupric oxide on platinum before the blowpipe dissolves it, forming a glass which is green while hot, and becomes white and opaque on cooling. (Berzelius.)

c. By the electrolytic method (I, 402), bluish-green, silky needles are obtained, from which hot water extracts carbonate of soda, and separates brown cupric carbonate. (Becquerel.)

C. *Borax* forms with cupric oxide in the outer blowpipe-flame, a clear bluish-green glass, which, when heated in the inner flame—especially with the addition of tin—is decolorized by formation of cuprous oxide, but at the moment of solidification, becomes scarlet-coloured and opaque. (Berzelius.)

D. With *Microcosmic Salt,* cupric oxide forms a bluish-green bead in the outer flame; and this, when heated in the inner flame, becomes opaque and red or brown-red at the moment of solidification, if the quantity of copper is considerable, but transparent and ruby-red if the quantity is small; with a still smaller quantity of copper, the red colour is not produced without the addition of tin; after a moment's exposure to the blast, the colourless glass solidifies on cooling to a red, opaque mass. (Berzelius.)

E. Hyposulphite of Cuprous Oxide and Soda.—*Cuproso-sodic Hyposulphite.—a. With* 3 *At. Copper-salt to* 2 *At. Soda-salt.*—A cold aqueous mixture of hyposulphite of soda and excess of cupric sulphate or acetate, forms in a short time a thick, egg-yellow, crystalline precipitate, which must be quickly collected on a filter, washed with water containing a small quantity of acetic acid, and rapidly dried in vacuo over oil of vitriol. The formation of this salt is attended with the production of sulphuric acid, a fact which may easily be verified by using acetate of cupric oxide in the preparation instead of sulphate. If the solutions are warm when mixed, a brown precipitate is formed; the yellow precipitate likewise turns brown if the filtering and washing are not quickly performed,—also when it is gently heated. Oil of vitriol decomposes the salt immediately; dilute sulphuric acid boiled with it liberates sulphurous

acid, throws down a precipitate of sulphide of copper, and acquires a greenish colour from dissolved cupric oxide. Cold hydrochloric acid converts the salt into a white mass without evolving even a trace of sulphurous acid; but on the application of heat, sulphurous acid is given off, sulphide of copper precipitated, and cuprous oxide dissolved. Caustic potash separates hydrated cuprous oxide from the salt; ammonia dissolves it, forming a brownish-yellow solution, which soon passes into dark blue when exposed to the air.—The salt dissolves sparingly in water, easily in aqueous hyposulphite of soda, but is insoluble in alcohol. (C. Lenz, *Ann. Pharm.* 40, 99.)

					Lenz.
$2NaO$	62·4	....	11·08	.....	11·20
$3Cu^2O$	216·0	....	38·34	.....	37·27
$5S^2O^2$	240·0	....	42·59	.....	42·67
$5HO$	45·0	....	7·99	.....	8·86
$2(NaO,S^2O^2)+3(Cu^2O,S^2O^2)+5Aq.$	563·4	....	100·00	.....	100·00

b. 1 *At. Copper-salt to* 3 *At. Soda-salt.*—From the solution of *a* in aqueous hyposulphite of soda, alcohol throws down a white salt. (C. Lenz, Rammelsberg, *Pogg.* 56, 323.)

$3NaO$	93·6	....	24·92	.....	23·93
Cu^2O	72·0	....	19·17	.....	20·30
$4S^2O^2$	192·0	....	51·12	.....	51·13
$2HO$	18·0	....	4·79	.....	4·64
$3(NaO,S^2O^2)+Cu^2O,S^2O^2+2Aq.$	375·6	....	100·00	.....	100·00

F. Sulphate of Cupric Oxide and Soda.—*Cuprico-sodic Sulphate.*—From a solution of blue vitriol and Glauber's salt, each of the salts crystallizes separately; but a solution of blue vitriol and bisulphate of soda yield's Glauber's salt and blue vitriol separately at first, but afterwards small crystals of the double salt united into a crust; they appear to contain 2 atoms of water. The salt may be easily dehydrated, fuses at a commencing red heat without losing acid, and on cooling solidifies in a blue mass which does not decrepitate like the potassic double salt. The salt deliquesces slowly in the air, and is decomposed by water into the two simple salts. (Graham, *Phil. Mag.* 4, 420.)

G. Dichloride of Copper and Sodium.—*Cuproso-sodic Chloride.*—Obtained by Becquerel (I. 401) by the electrolytic method in transparent and colourless octohedrons, which turned green when the experiment was continued for a considerable time.—Dichloride of copper dissolves abundantly in solution of common salt, forming a colourless liquid, which gives an orange-yellow precipitate with alkalis and white with ferrocyanide of potassium. (Boussingault, *Ann. Chim. Phys.* 51, 352.)

Copper and Barium.

A. Alloy of Copper and Barium?—*a.* Clarke (*Gilb.* 62, 374) obtained a golden yellow alloy by heating copper and barium together before the oxy-hydrogen blowpipe.—*b.* Lampadius (*Schw.* 15, 146) by heating to whiteness 4 parts of baryta with 4 copper and 1 charcoal-dust, obtained a substance which crumbled to pieces when exposed to the air, being resolved into baryta and cupric oxide. (?)

B. *Cupric Oxide with Baryta?* — Cupric oxide precipitated from its solution by baryta, carries down with it 1 or 2 per cent. of baryta, which cannot be extracted by water. (Grouvelle.)

C. SULPHIDE OF COPPER AND BARIUM.—10 parts of ignited blue vitriol heated to whiteness in a charcoal crucible with 5 parts of sulphate of baryta, yield 8·1 parts of a fused, compact, brittle, distinctly laminar, lead-grey metallic sulphide containing a few grains of copper, and efflorescing rapidly in the air.

D. DICHLORIDE OF COPPER AND BARIUM.—Becquerel obtained this salt by the electrolytic method. (I. 400.)

COPPER AND CALCIUM.

Cupric Oxide with Lime? — Lime withdraws cupric oxide from its solution in ammonia. (Kuhlmann, *Ann. Pharm.* 41, 227.)

B. SULPHIDE OF COPPER AND CALCIUM.—10 parts of anhydrous cupric sulphate and 5 parts of crystallized gypsum, heated to whiteness in a charcoal crucible, yield 6·47 parts of a well-fused, blistered, lead-grey metallic sulphide, with granules of copper imbedded in it; when this substance is treated with acetic acid, sulphuretted hydrogen is given off, and nothing but the lime is dissolved. (Berthier.)

C. One atom of fluorspar and 1 At. blue vitriol heated together to bright redness, form a thin liquid which yields on cooling, a compact, white mass (with a slight tinge of brick-red proceeding from a small quantity of liberated cupric oxide), which has a shining, crystallo-granular fracture, and from which water extracts cupric sulphate. But at a stronger red heat, the sulphuric acid goes off in a decomposed form, and there remains a mixture of fluorspar and cupric oxide. (Berthier, *Ann. Chim. Phys.* 43, 300.)

COPPER AND MAGNESIUM.

A. SULPHIDE OF COPPER AND MAGNESIUM.—Obtained by heating blue vitriol and sulphate of magnesia to whiteness in a charcoal crucible. The fused mass contains magnesia in a state of mechanical mixture. (Berthier.)

B. SULPHATE OF CUPRIC OXIDE AND MAGNESIA.—Crystallizes in the form of ferrous sulphate with 7 atoms of water, if the magnesia-salt is in excess, and in the form of cupric sulphate with 5 atoms of water, if the copper-salt is in excess. (Mitscherlich.) Sulphate of magnesia dissolves quickly in a saturated solution of blue vitriol, and the undissolved portion of the magnesia-salt is gradually converted into the double salt. (Karsten.)

C. SULPHATE OF CUPRIC OXIDE, MAGNESIA, AND AMMONIA.—Separates from an aqueous mixture of sulphate of magnesia and ammonia,

and sulphate of cupric oxide and ammonia, in pale blue crystals, having the form of sulphate of magnesia and ammonia. (Bette, *Ann. Pharm.* 14, 284.)

$$(NH^4O, SO^3 + MgO, SO^3 + 6Aq.) + (NH^4O, SO^3 + CuO, SO^3 + 6Aq.)$$

					Bette.
$2NH^3$	34	....	8·95	.....	9·20
MgO	20	....	5·25	.....	4·54
CuO	40	....	10·53	.....	10·78
$4SO^3$	160	....	42·11	.....	40·96
14HO	126	....	33·16	.....	34·52
	380	....	100·00	.....	100·00

Copper and Aluminum.

A. Aluminate of Cupric Oxide.—Precipitated on mixing B with ammonia, an excess of that reagent not being able to extract the cupric oxide.

B. Fluoride of Aluminum and Copper. — CuF, Al^2F^3. — Pale bluish-green [hydrated ?] needles, very slowly but completely soluble in water. (Berzelius.)

Copper and Zirconium.

Zirconate of Cupric Oxide.—When a salt of zirconia mixed with a cupric salt is precipitated by ammonia in excess, the zirconia carries down the cupric oxide, which cannot be extracted by ammonia, and forms with it a sky-blue precipitate, which becomes emerald-green after ignition. While yet moist, it gives up part of its cupric oxide to carbonate of ammonia, but is not completely decolorized by it. The cupric oxide is not separated by oxalic or acetic acid. (Berthier, *Ann. Chim. Phys.* 49, 196.)

Copper and Silicium.

A. Silicide of Copper.—*a.* Silicium may be fused into a ductile bead with copper before the blowpipe, and the alloy thus formed leaves a siliceous skeleton when dissolved in acids. (Berzelius, *Pogg.* 1, 220.)—*b.* By heating copper to intense whiteness with silica and charcoal powder, a compound is obtained containing a small quantity of carbon and perfectly soluble in acids; the solution when evaporated yields 5 per cent. of silica. (Berzelius, *Gilb.* 36, 100.)

B. Silicate of Cupric Oxide, or Cupric Silicate.—*a. Monosilicate.*—*α. Mono-hydrated.—Emerald Copper*, or *Dioptase.*—Crystalline system the rhombohedral. Primary form an obtuse rhombohedron; *Fig.* 141, $r^3 : r^5 = 126° 17'$; less obtuse rhombohedron; $r^3 : r^5 = 95° 48'$, often with truncated lateral edges. *Fig.* 145. Specific gravity 3·278. Of the hardness of apatite.—Transparent, emerald-green. Turns black, from loss of water, in the outer flame (green in the inner: *Kobell*), and red in the inner, without fusing. With a small quantity of carbonate of soda on charcoal, it yields a turbid red glass, together with a bead of copper; with a

E. and F. Cuprous oxide forms with glass-fluxes, sometimes blood-red and transparent, sometimes brown-red, opaque masses. Cupric oxide imparts to glass-fluxes a blue or greenish-blue colour without diminishing their transparency.

Copper and Titanium.

Fluoride of Titanium and Copper.—*Hydrated.*—Formed by mixing the two simple salts. Long, pale bluish-green needles, which, with the exception of the colour, perfectly resemble the fluoride of titanium and magnesium. (III. 487.) They dissolve in pure water with partial decomposition, easily and completely in acidulated water. (Berzelius.)

Copper and Tungsten.

A. Tungstide of Copper.—Brownish copper-coloured, porous, tolerably extensible.

B. Tungstate of Cupric Oxide, or Cupric Tungstate.—*a. Monotungstate.*—Cupric salts throw down from monotungstate of potash a light green powder, which turns yellowish-brown, and gives off its water when heated—fuses at a red heat—and on cooling, solidifies in a chocolate-coloured, crystalline mass, having in its cavities crystalline geodes, which, when examined by the microscope, are found to consist of transparent six-sided prisms of a deep wine-yellow colour. The unignited salt is insoluble in water, but after continued washing, passes through the filter and renders the filtrate milky. It dissolves in phosphoric acid, acetic acid, and ammonia, but not in oxalic acid. (Anthon.)

	Ignited.			Anthon.		*Dried in the air.*			Anthon.
CuO	40	....	25	....	25·84	CuO	40	....	22·47	....	23
WO^3	120	....	75	....	74·16	WO^3	120	....	67·42	....	66
						2HO	18	....	10·11	....	11
CuO,WO^3	160	....	100	....	100·00	+2Aq.	178	....	100·00	....	100

b. Bitungstate.—The light green precipitate obtained with an alkaline bitungstate, turns brown and gives off water when ignited, fusing partially, throwing out cauliflower-like excrescences, and finally assuming a dark lead-grey colour. The unignited salt when digested in nitric acid, swells up in a gelatinous form, but does not dissolve. It is likewise insoluble in water, but soluble in ammonia. (Anthon, *J. pr. Chem.* 9, 346.)

	Ignited.			Anthon.		*Dried in the air.*			Anthon.
CuO	40	....	14·29	....	13·64	CuO	40	....	12·66	....	12
$2WO^3$	240	....	85·71	....	86·36	$2WO^3$	240	....	75·95	....	76
						4HO	36	....	11·39	....	12
$CuO,2WO^3$	280	....	100·00	....	100·00	+4Aq.	316	....	100·00	....	100

C. Cupric Sulphotungstate.—CuS,WS^3.—Liver-coloured precipitate, which assumes a dark brown colour when collected on the filter. (Berzelius.)

Copper and Molybdenum.

A. Molybdide of Copper.—Pale copper-red; malleable if the molybdenum is not in excess. (Hielm.)

B. Molybdate of Cupric Oxide, or Cupric Molybdate.—Yellowish-green precipitate, sparingly soluble in water, decomposed by acids and by alkalis. (Berzelius.)

C. Cupric Sulphomolybdate.—CuS,MoS^3.—Black-brown precipitate. (Berzelius.)

D. Cupric Persulphomolybdate.—CuS,MoS^4.—Dark red precipitate, which turns brown when collected on the filter. (Berzelius, *Pogg.* 7, 287.)

Copper and Vanadium.

Vanadiate of Cupric Oxide, or Cupric Vanadiate.—*a. Monovanadiate.*—An aqueous mixture of a copper-salt with an alkaline monovanadiate, yields, on the addition of alcohol, a yellow precipitate, which is soluble in water, and when the water is evaporated, remains in the form of a dark yellow, amorphous mass.—*Bivanadiate.*—Separates gradually from an aqueous mixture of blue vitriol and bivanadiate of potash, in the form of a yellow, crystalline crust. (Berzelius.)

Volborthite appears to be a *basic Vanadiate of Cupric Oxide.* Olive-green needles united in tufts, yielding a yellowish-green powder. Specific gravity 3·55. Turns black and gives off water when heated. Fuses easily on charcoal without fume or deposit, and when more strongly heated, solidifies in the form of a graphitic slag, containing granules of metallic copper. With carbonate of soda on charcoal, it immediately yields copper. Dissolves in borax or microcosmic salt, producing a beautiful green colour. Heated with not too large a quantity of microcosmic salt on platinum wire, it forms a green glass in the inner flame and yellow in the outer, these colours becoming brighter on cooling; with tin, the bead becomes red-brown and opaque.—Dissolves in hydrochloric acid with evolution of chlorine; the solution in moderately strong nitric acid, when left over-night, deposits brick-red vanadic acid. Insoluble in water. (Hess, *J. pr. Chem.* 14, 52.)

Copper and Chromium.

Chromate of Cupric Oxide, or Cupric Chromate.—*a. With a great excess of Base?*—Prepared as a fine green colour by the following methods: 1. By adding 2 parts of pearl-ash and 1 part of chalk to a solution of 48 pts. blue vitriol and 2 pts. bichromate of potash, pressing the precipitate to expel the greater part of the water, and then drying and reducing it to powder. The colour is not so fine as that of Schweinfurt green. (Juch, *J. pr. Chem.* 29, 204.) [According to these proportions, the precipitate might contain 2 At. cupric oxide to 1 At. chromic acid. The prescribed quantity of cupric oxide appears to be much too large.]—2. By gradually adding ammonia to a solution of 2 pts. blue

vitriol and 1 pt. bichromate of potash, at a temperature between 20° and 30°, till the red-brown precipitate [of salt *b ?*] produced at first, begins to turn green; if too much ammonia were added, the precipitate would dissolve and form a green solution. When the temperature and the quantity of ammonia are rightly adjusted, the colour is very brilliant; the precipitate produced at too high or too low a temperature loses all its chromic acid during washing, and is converted into the blue hydrated oxide. (Leykauf, *J. pr. Chem.* 22, 448.)

b. Basic ?—1. Monochromate of potash forms with neutral copper-salts, a yellowish-brown precipitate, becoming chestnut-brown when dry. (Vauquelin.) After complete washing with hot water, the salt assumes a lighter colour, and when perfectly dry, becomes yellowish-brown, like hydrated ferric oxide. (Böttger.) When monochromate of potash is dropped into a boiling solution of blue vitriol, the blue colour changes through green and yellow to red, whereupon a brown precipitate is produced, which finally becomes dark red-brown. (Bensch, *Pogg.* 55, 97.) Boiling water extracts from the precipitate a large quantity of bichromate of potash. (Gm.) 2. By treating carbonate of cupric oxide with excess of chromic acid, the salt is obtained with a yellowish-brown colour. (Böttger.) Potash or soda withdraws all the chromic acid from this salt, separating the blue hydrated oxide in the cold, and the black anhydrous oxide at higher temperatures. Dissolves easily in dilute nitric acid, and likewise in ammonia, in which it forms a green solution.

Normal salt ?—Bichromate of potash does not precipitate cupric salts. The solution of hydrated cupric oxide in aqueous chromic acid yields by slow evaporation—during which it effloresces—transparent green crystals, having the form of blue vitriol and a density of 2·262; they contain 33·5 per cent. of water. These crystals turn white when dehydrated, and if subsequently moistened with water, become very hot and recover their green colour. They are easily soluble in water, but insoluble in alcohol. (Kopp, *Ann. Pharm.* 42, 98.) The author did not succeed in obtaining this salt. The carbonate of cupric oxide dissolved sparingly in aqueous chromic acid, and the brownish-yellow solution yielded on evaporation a non-crystalline residue, from which water extracted chromic acid with a small quantity of cupric oxide, leaving a dark-green powder. (Gm.)

B. Cupro-chromate of Ammonia.—Monochromate of cupric oxide yields, with aqueous ammonia, a beautiful dark green solution, which does not lose its colour by exposure to light, and again yields cupric chromate, both on evaporation and on the cautious addition of acid. (Vuaflart, *J. Pharm.* 10, 607.) The green solution, if covered with strong alcohol, deposits cupro-chromate of ammonia, in the form of a dark green powder, which must be collected on a filter, and then washed with alcohol. It decomposes when kept for some time. In hot water it is resolved into chromate of ammonia, which dissolves, and a light green powder, which evolves ammonia when treated with potash, and is therefore a basic double salt. (R. Böttger, *Beitr.* 2, 77.)

Copper and Uranium.

Uranico-cupric Phosphate.—*Chalkolite, Kupferuranglimmer.*—Isomorphous with *Calcareous Uranite.* (IV. 191.) Siskin-green. Before the blowpipe it behaves like calcareous uranite, but when heated on

precipitated by a solution of arsenious acid in excess of carbonate of potash, so that carbonate of cupric oxide becomes mixed with the precipitate. To prepare *Mineral-green*, 100 parts of blue vitriol are mixed, first with a solution of 10 or 12 parts of arsenious acid, and then with excess of caustic potash-ley, prepared from 90 parts of pearl-ash and 80 of lime. This pigment is dark green, and has a conchoidal fracture. (Gentle.)

(With respect to *Schweinfurt green*, *Vienna green*, and *Mitis-green*, vid. *Acetic Acid*.)

b. Acid Arsenite.—The solution of cupric carbonate in excess of aqueous arsenious acid is not precipitated, either by acids or by alkalis; when evaporated, it leaves a yellowish-green salt. (Berzelius.)

C. Arseniate of Cupric Oxide, or Cupric Arseniate.—*a. Octobasic?—Euchlorose, Copper-mica.*—Crystalline system the rhombohedral. Acute rhombohedrons considerably truncated; *Fig.* 153; $r^3 : r^5 = 68° 41'$. Cleavage distinct parallel to *p*. Specific gravity varying from 2·5 to 2·6. Soft, transparent, emerald-green. Decrepitates strongly before the blowpipe, the flame being coloured green by the detached particles. On charcoal it fuses without detonation, but with emission of arsenical fumes, and forms a grey, brittle, metallic globule, which, by a second fusion, with the addition of carbonate of soda, is converted into malleable copper. (*v.* Kobell.)

	Euchlorose.			Chenevix.	Vauquelin.
8CuO	320		58·93	58	39
AsO^5	115		21·18	21	42
12HO	108		19·89	21	17
$8CuO, AsO^5 + 12Aq$	543		100·00	100	98

b. Pentabasic.—*α. Bi-hydrated.—Erinite.*—Formed of concentric scales with rough surfaces formed by the ends of very small crystals. Specific gravity 4·043. Dull; translucent on the edges; emerald-green inclining to apple-green. (Turner, *Edinb. J. of Sc.* 9, 93; also *Pogg.* 14, 228.)

		Erinite.		Turner.
5CuO	200		60·06	59·44
AsO^5	115		34·54	33·78
2HO	18		5·40	5·01
Al^2O^3				1·77
$5CuO, AsO^5 + 2Aq$	333		100·00	100·00

β. Penta-hydrated.—Aphanese, Strahlenkupfer.—Under this name are included two minerals, in one of which two-thirds of the cupric oxide appear to be replaced by ferrous oxide. The supposition of Chenevix (*Phil. Trans.* 1801, 201; also *A. Gehl.* 2, 131), that the iron in this mineral is in the form of ferric oxide, is improbable.

	At.		*Aphanese.*			Chenevix.
CuO	5		200		55·56	54
FeO						
AsO^5	1		115		31·94	30
HO	5		45		12·50	16
$5CuO, AsO^5 + 5Aq$			360		100·00	100

	At.		*Aphanese.*				Chenevix.
CuO	2	....	80	....	22·99	.....	22·5
FeO	3	....	108	....	31·03	Fe^2O^3	27·5
AsO^5	1	....	115	....	33·05	.....	33·5
HO	5	....	45	....	12·93	.....	12·0
Quartz		....		....		.....	3·0
			348	....	100·00	.....	98·5

γ. *Deca-hydrated.—Leirochroite, Kupferschaum.*—Formed of diverging fibres. Specific gravity 3·09. Very soft; translucent; of a light verdigris-green colour. Decrepitates strongly in the flame of a candle, colouring it green by the scattered powder. When held in the forceps, and heated by the blowpipe-flame, it turns black, and fuses into a steel-grey bead. On charcoal it fuses quietly, exhibiting a slight intumescence only after a long-continued fusion; it then likewise emits an odour of arsenic, and on cooling yields a non-crystallizing globule, which becomes continually more difficult of fusion, and acquires a brownish surface. With carbonate of soda it yields an imperfectly-fused mass, in which metallic globules are enclosed. Evolves carbonic acid slowly when immersed in cold hydrochloric acid, rapidly in the same acid when heated. Dissolves in ammonia, leaving a residue of carbonate of lime (*v.* Kobell, *Kastn. Arch.* 23, 96; also *Pogg.* 18, 253).

	At.		*Leirochroite.*			Or? At.					Kobell.
CuO	5	....	200	....	49·38	5	....	200	....	43·95	.... 43·88
AsO^5	1	....	115	....	28·40	1	....	115	....	25·28	.... 25·01
HO	10	....	90	....	22·22	10	....	90	....	19·78	.... 17·46
CaO, CO^2		....		....		1	....	50	....	10·99	.... 13·65
$5CuO, AsO^5 + 10Aq.$			405	....	100·00			455	....	100·00	.... 100·00

In the second calculation, the carbonate of lime is estimated as an essential constituent; according to this, the mineral will be: $CaO, CO^2 + 5CuO, AsO^5 + 10Aq$.

c. *Quadrobasic.*—α. *Mono-hydrated.— Olivenite.*—Crystalline system the right prismatic. *Fig.* 54 and other forms: $u : u' = 87° 30'$; $i : i'$ *behind* $= 110° 50'$. Specific gravity from 4·28 to 4·4. Hardness equal to that of calcspar. (Haidinger.) Transparent, and of an olive-green colour inclining to yellow and brown.—When heated in a glass tube, it gives off a small quantity of water, but no arsenious acid. Held in the forceps before the blowpipe, it fuses, imparts a pale blue colour to the flame, and on cooling, crystallizes in the form of a black brown, radiated mass, having an adamantine lustre, and covered on the surface with a network of prismatic crystals. On charcoal, it deflagrates, emits a strong odour of arsenic, and yields a somewhat ductile regulus, brownish on the outside and white in the middle. (Kobell.) The mineral is soluble in nitric acid and in ammonia.

	Olivenite, from Cornwall.				Kobell.		Richardson.		Klaproth.		Chenevix.
28CuO	1120·0	....	57·60	....	56·43	....	56·2	....	50·62	....	60·0
$6AsO^5$	690·0	....	35·48	....	36·71	....	39·9	....	45·00	....	39·7
PO^5	71·4	....	3·68	....	3·36						
7HO	63·0	....	3·24	....	3·50	....	3·9	....	3·50		
$^{\cdot}CuO, (AsO^5; PO^5) + Aq.$	1944·4	....	100·00	....	100·00	....	100·0	....	99·12	....	99·7

β. Hepta-hydrated.—Euchroite.—Crystalline system the right prismatic. *Fig.* 74, together with *p*-faces and others. Transparent, and of a light emerald-green colour. (Haidinger.) At a temperature somewhat below redness it gives off its water without decrepitation, and becomes dingy green and friable. On platinum in the outer blowpipe-flame it does not fuse till heated above the melting point of glass; crystallizes to a greenish-brown mass on cooling. On charcoal it fuses readily, deflagrating immediately, and giving off an odour of arsenic; after long-continued blowing, it yields a globule of metallic copper. Heated to redness with charcoal powder in a glass tube, it yields a sublimate of arsenic and arsenious acid. Dissolves easily in nitric acid.

	Euchroite.				Turner.
$4CuO$	160	....	47·34	....	47·85
AsO^5	115	....	34·02	....	33·02
$7HO$	63	....	18·64	....	18·80
$4CuO, AsO^5 + 7Aq.$	338	....	100·00	....	99·67

γ. Deca-hydrated.—Liroconite.—Crystalline system the right prismatic; *Fig.* 63, with the *y*-faces enlarged so as to obliterate the *p*-face; $u : u' = 119° 45'$; $y : y$, *behind*$=108° 1'$. Specific gravity 2·92. Harder than gypsum. Transparent, and of a sky-blue colour inclining to verdigris-green. When heated it does not decrepitate, but turns smalt-blue, afterwards light green, and at a red heat greyish-green. When held in the forceps, it colours the blowpipe-flame bluish-green. On charcoal it fuses imperfectly and with slight intumescence, forming a brownish slag which contains white granules of metal. With carbonate of soda it yields a semi-malleable button of copper containing arsenic. (Kobell, *Kastn. Arch.* 23, 100; Trolle Wachtmeister, *Pogg.* 25, 305.)

	Liroconite.				Trolle Wachtmeister.		Chenevix.
$20CuO$	800·0	....	37·88	.....	37·84	....	49
$4AsO^5$	460·0	....	21·79	.....	22·35	....	14
PO^5	71·4	....	3·38	.....	3·88	....	
$55HO$	495·0	....	23·44	.....	23·91	....	35
$4Al^2O^3$	205·6	....	9·73	.....	8·63	....	
Fe^2O^3	80·0	....	3·78	.....	3·65	....	
	2112·0	....	100·00	.....	100·26	....	98

$4CuO(AsO^5; PO^5) + 10\,Aq. + (Al^2O^3; Fe^2O^3), Aq.$ The hydrate of alumina and hydrated ferric oxide ought perhaps to be regarded as accidental.

d. Terbasic.—Precipitated on mixing a cupric salt with diarseniate of ammonia, potash, or soda, the liquid acquiring an acid reaction. (Mitscherlich.)—Pale bluish-green precipitate. Gives off water when heated, and, at a higher temperature, fuses into an olive-green mass, without decomposition, excepting where it is in contact with the charcoal. (Proust.) Before the blowpipe on charcoal it yields a button of copper. (Simon.) Insoluble in water, but soluble in the stronger acids and in ammonia. Sulphurous acid likewise dissolves it without formation of cuprous oxide. (A. Vogel.)

Whether the precipitate which free arsenic acid forms in acetate of cupric oxide, and the bluish-white powder produced by the action of arsenic acid on copper in the air, likewise belong to this head, is not yet clearly ascertained.

Chenevix obtained blue rhombohedral crystals, by mixing nitrate of

cupric oxide with arseniate of ammonia, separating the liquid from the precipitate, and mixing it with alcohol after evaporation.

D. Cupric Sulpharsenite.—*a. Twelve-basic.*—$12CuS,AsS^3$. — Remains undissolved in the form of a red-brown mass, when hydrated cupric oxide is added to monobasic sulpharseniate of potassium, till the colour of the former is no longer altered (IV. 293).

b. Terbasic.—$3CuS, AsS^3$.—On adding hydrochloric acid to the hyacinth-red solution *a*, this compound is precipitated in light brown flakes, while chloride of potassium and hydrochlorate of arsenious acid remain in the liquid.

c. Bibasic.—$2CuS,AsS^3$.—Formed by precipitating a cupric salt with bibasic sulpharsenite of sodium.—Black-brown precipitate, which acquires a metal-grey aspect by trituration. When subjected to distillation, it first gives off sulphur, then tersulphide of arsenic, and leaves a semi-fused, tumefied metal-grey substance, probably a compound of bisulphide of arsenic with disulphide of copper: *Cuprous Hyposulpharsenite.* (Berzelius, *Pogg.* 7, 148.)

E. Cupric Sulpharseniate.—$2CuS,AsS^5$.—Sulpharseniate of sodium dissolved in water yields with cupric salts a dark brown precipitate, which turns black in drying. This compound is likewise precipitated on passing sulphuretted hydrogen through acid solutions containing arsenic acid and cupric oxide; if the arsenic acid is in excess, the brown sulphur-salt is first precipitated, and then the yellow pentasulphide of arsenic. (Berzelius, *Pogg.* 7, 22.) When a precipitate of this kind is treated with hydrosulphate of ammonia, not only is the sulphide of arsenic dissolved, but likewise by its intervention, a large portion of the sulphide of copper. (Anthon, *Repert.* 76, 125.) Very dilute ammonia likewise extracts the sulphide of arsenic, stronger ammonia acquires a brown tint by taking up some of the sulphide of copper. (Gm.)

Copper and Antimony.

A. Antimonide of Copper.—Formed by fusing copper with antimony, combination then taking place without visible combustion,—or with sulphide of antimony, whereupon sulphide of copper is produced at the same time.—0·15 per cent. of antimony makes the copper somewhat brittle when cold, and very brittle at a red heat. (Karsten.)

B. Antimonic Oxide with Cuprous Oxide.—Called copper-mica by the workmen.—This compound is found in refined copper prepared from antimonial ores, and renders it more cold-short than red-short. When copper of this description is dissolved in cold or slightly warmed nitric acid, the compound is left behind in very thin, regular, six-sided laminæ, which are translucent and of a golden yellow colour. When heated, they become for the time brown and opaque. In the flame of Newman's oxy-hydrogen blowpipe, they fuse into a black-brown glass; with borax they exhibit slight intumescence, and form a yellowish-brown glass, which turns greenish-blue when mixed with nitre. Strong hydrochloric acid dissolves them more completely than any other acid. (Hausmann & Stromeyer, *Schw.* 19, 241.)

	Copper-mica.			Stromeyer.	After deducting the remainder.
$3Cu^2O$	216	58·54		50·50	57·68
SbO^3	153	41·46		37·05	42·32
PbO				4·05	
AgO				0·16	
Fe^2O^3				0·07	
SiO^3 and Al^2O^3				1·58	
$3Cu^2O, SbO^3$	369	100·00		93·41	100·00

Nickeliferous Copper-mica.—Obtained from copper smelted at Goslar. After the copper has been treated with dilute nitric acid, the copper-mica is freed from arsenical oxide of antimony—proceeding from antimonide of copper previously contained in the copper, and decomposed by the nitric acid—by digesting it in a mixture of hydrochloric and tartaric acid. In this manner, 100 parts of highly micaceous copper yield 4·16 parts of pure copper-mica.—Pale greenish-yellow, translucent, strongly lustrous, regular six-sided laminæ, which assume a transient yellow colour when heated. This compound neither fuses nor suffers any alteration at a red heat. With carbonate of soda on charcoal, it yields a white brittle metal, and covers the charcoal with antimonic oxide. Heated in the outer blowpipe-flame with borax or microcosmic salt, it dissolves immediately and forms a light green glass. It is scarcely attacked by acids, excepting by concentrated hydrochloric acid, which dissolves it after long boiling. When hydrogen gas is passed over 100 parts of red-hot copper-mica, a quantity of water is obtained, corresponding to 18·19 per cent. of oxygen. (In this reaction, 2·55 parts of the mica—that which contains only nickel and no copper—appear to escape decomposition.) The residue is baked together, but still retains the form of laminæ; it may be decomposed by nitric acid or by chlorine; in either case, the pure nickel-mica remains undecomposed. (Borchers, *Pogg.* 41, 335.)

	Nickeliferous Copper-mica.			Borchers.
7Cu	224·0		36·10	34·27
5Ni	147·5		23·77	23·36
1Sb	129·0		20·79	20·53
15O	120·0		19·34	18·19
Undecomposed Mica				2·55
	620·5		100·00	98·90
Or:				Borchers.
7CuO	280·0		45·13	44·28
5NiO	187·5		30·21	30·61
SbO^3	153·0		24·66	25·11
	620·5		100·00	100·00

Hence it would appear that this nickeliferous copper-mica contains not cuprous but cupric oxide. (Borchers.)

C. Cupric Antimonite.—Pale grass-green; becomes pistachio-green when heated; glows and turns white at a stronger heat. Insoluble in water. (Berzelius.)

D. Cupric Antimoniate.—Formed by precipitating blue vitriol with antimoniate of potash. Pale green, crystalline powder, which becomes blue-green when dry, and when gently heated, gives off 19·5 per cent. of

water, and assumes a greenish-black colour. At a red heat, it glows and becomes greenish white, after which it is not attacked either by acids, or in the humid way, by alkalis. When heated upon charcoal it deflagrates slightly, and is easily reduced to pale red antimonide of copper. Insoluble in water. (Berzelius.)

E. Cuprous Sulphantimonite. — *Antimonial Copper-glance.* — Crystalline system, the right prismatic. Fig. 80, without the *i*- and *m*-faces; $n' : n = 135° 12'$; $u' : u = 111°$; $u : t = 129° 30'$. Cleavage distinct parallel to the *p*-face, which is very much enlarged; less distinct parallel to *p*. (G. Rose.) Specific gravity 4·478; harder than calcspar; strongly lustrous; lead-grey inclining to iron-black; yields a black powder. Before the blowpipe, it decrepitates strongly and splits into laminæ—fuses easily—covers the charcoal with antimonic oxide, and ultimately yields a brittle metallic globule. With carbonate of soda, it yields a red-grey brittle globule, which, by continued blowing, is converted into metallic copper. (Zincken, *Pogg.* 35, 357.)

					H. Rose.
2Cu	64	....	24·90	.....	24·46
Sb	129	....	50·20	.....	46·81
4S	64	....	24·90	.....	26·34
Pb		....		.....	0·56
Fe		....		.....	1·39
Cu^2S, SbS^3	257	....	100·00	.....	99·56

F. Cupric Sulphantimoniate.—Formed by mixing the solution of Schlippe's salt with a quantity of blue vitriol not sufficient to decompose it completely. The precipitate heated in a retort gives off sulphur, and leaves 80·98 per cent. of a fused residue probably containing $3Cu^2S$, $2SbS^3$. (Rammelsberg, *Pogg.* 52, 226.)

					Rammelsberg.
3Cu	96	....	27·19	.....	25·50
Sb	129	....	36·55	.....	35·04
8S	128	....	36·26	.....	36·80
$3CuS, SbS^5$	853	....	100·00	.....	97·34

If an excess of blue vitriol is used in the precipitation, and the liquids are mixed cold, a precipitate of variable composition is obtained; but on boiling the mixture (as in preparing the corresponding lead-compound) the precipitate is completely converted into $8CuS,SbO^3$. This substance, when treated with caustic potash, gives up its antimonic acid, and is converted into protosulphide of copper. When heated to redness in a retort, it fuses completely, gives off sulphuric acid and antimonic oxide, and leaves a blackish-grey metallic mass, apparently composed of $6(Cu^2S)$, SbS^3. (Rammelsberg.) The decomposition is probably as follows:

$$3(8CuS, SbO^5) = 2(6Cu^2S, SbS^3) + SbO^3 + 6SO^2.$$

G. Antimonide of Copper and Potassium. — Formed by roasting 4 parts of tartar on a piece of earthenware, till only 2 parts remain, and fusing the residue for 2 hours in a powerful air-furnace, with 2 parts of powdered antimony, 2 copper-filings and 1 charcoal.—The alloy is violet, has a very laminar fracture, yields slightly to the hammer and is slightly volatile. Small pieces of it move rapidly on mercury, the surface of which is covered with a small quantity of water. (Serullas, *Ann. Chim. Phys.* 21, 199.)

Copper and Tellurium.

A. Telluride of Copper.—Pale red. (Berzelius.)

B. Cupric Tellurite.—Siskin-green precipitate which is insoluble in water, turns black and gives off its water when heated, fuses easily, and solidifies on cooling to a black mass having a conchoidal fracture, and yielding a greenish-brown powder. Before the blowpipe on charcoal, it is reduced, with deflagration, to pale red telluride of copper. It may be fused with 1 At. cupric oxide, the product being a black mass having an earthy fracture. (Berzelius.)

C. Cupric Tellurate.—*a. Monotellurate.*—Bulky, slightly translucent, sea-green precipitate. — *b. Bitellurate.* Pale green precipitate. (Berzelius.)

D. Cupric Sulphotellurite. — $3CuS,TeS^2$. — Brown precipitate, black after drying, giving off sulphur by distillation, and leaving a metal-grey residue. (Berzelius.)

Copper and Bismuth.

A. Alloy of Bismuth and Copper.—Combination between these two metals takes place at a temperature below the melting point of copper. An alloy of 1 pt. copper and 2 bismuth begins to expand a considerable time after solidification. An alloy of 1 pt. copper and 4 bismuth throws out nodules and spherules as it solidifies—has a fine red colour and broadly laminar texture—but contains small globules enclosed within the laminæ. (Marx, *Schw.* 58, 470.)—Copper alloyed with small quantities of bismuth remains ductile at ordinary temperatures; but when hammered, it becomes so hard and brittle as to require a second ignition; and if the quantity of bismuth amounts to even 0·6 per cent., the alloy cracks on the edges when hammered at a red heat. (Karsten.)

B. Sulphide of Bismuth and Copper. — *Copper-bismuth-glance* or *Bismuth-copper-ore.*—In indistinct prisms and radiating; soft and pliable. Has a lead-grey colour, and yields a black powder.—When heated in an open tube, it gives off sulphur and a white sublimate, and afterwards enters into ebullition. Fuses easily before the blowpipe, covering the charcoal with a yellow deposit. With carbonate of soda, it yields a large button of copper. (Berzelius.) Dissolves in nitric acid with separation of sulphur. The following analysis does not admit of reduction to a formula.

	Klaproth.
Cu	34·66
Bi	47·24
S	12·58
	94·48

Copper and Zinc.

A. Alloys of Copper and Zinc.—*Brass, Tombac, Pinchbeck, Prince's Metal, Similor, Mannheim Gold, Aurum mosaicum,* according to the

proportions and purity of the ingredients.—*Preparation.* 1. By adding zinc to melted copper, whereupon some degree of explosion and scattering of the mass is produced. (Berzelius; A. Vogel; *J. pr. Chem.* 6, 344.) Or by fusing the metals together in a covered crucible, the zinc being placed below, and the copper in small pieces at top. For brass the proportion is 7 pts. copper to 3 zinc. Part of the zinc always burns away. The fusion is performed in crucibles, seven of which are usually placed in a circular air-furnace.—2. By igniting copper in small pieces with zinc-oxide and charcoal powder. In this older method of making brass, roasted native calamine or furnace-calamine is ignited in covered crucibles with charcoal powder and copper, the latter being cut into small pieces or granulated.—3. Copper exposed at a red heat to vapours of zinc is completely penetrated by them, but does not lose its form.—*Lyons Gold-lace* is prepared by exposing rods of copper to the vapour of zinc, till they are converted into brass on the surface, and then drawing them out into wire. A copper coin placed in a crucible above a mixture of zinc-oxide and charcoal, and moderately ignited, is converted into brass without obliteration of the device.—4. By precipitation.—In England, *Spurious gold-wire* is prepared by boiling copper-wire previously cleaned with nitric acid, with hydrochloric acid, cream of tartar, and a mixture of 1 pt. zinc and 12 mercury. (*Gilb.* 49, 301.)—When blue vitriol, dissolved in 20 parts of water, is precipitated by zinc, the black flakes at first precipitated are an alloy of copper and zinc. (Bucholz and Meissner, *N. Tr.* 3, 2, 87.)

Copper alloyed with a small quantity of zinc exhibits a paler red and yellowish red colour; a larger quantity renders it yellow, the colour being brightest when the two metals are united in equal parts; a still greater quantity of zinc makes it white. (Lewis.) In certain proportions, the alloy of copper and zinc is more ductile at ordinary temperatures than pure copper, but generally brittle at a red heat. Very small quantities of zinc do not impair the ductility of copper at ordinary temperatures, excepting that, when thus alloyed, it sooner becomes hard and brittle by hammering, and therefore requires to be oftener heated to redness; but even 0·6 per cent. of zinc is sufficient to cause copper to crack when hammered at a red heat. (Karsten.)—The most ductile of all the alloys of copper and zinc are those which contain 84·5 per cent. of copper to 15·5 of zinc (tombac), and 71·5 copper to 28·5 zinc (brass).—The alloy formed of equal weights of the two metals cracks in rolling. An excess of zinc renders the alloy brittle, the most brittle of all being that which contains 1 At. copper with $1\frac{1}{2}$ to 2 At. zinc. (Karsten.)—Small quantities of lead diminish the ductility of the alloy; tin increases its hardness. (Karsten.)

All alloys in which the amount of zinc does not exceed 50 per cent. exhibit the reaction of copper towards acids and in the voltaic circuit, and they do not precipitate the salts of copper. But alloys containing excess of zinc decompose copper-salts, being thereby converted into perfectly pure copper; they likewise dissolve completely in acids which have no action on copper alone, the solution taking place the more quickly as the excess of zinc is greater. If the quantity of acid is insufficient to dissolve the whole, the copper first dissolved is reprecipitated, the liquid at length retaining nothing but zinc. (Karsten.) Brass turns red when rubbed with hydrochloric acid, because the acid dissolves the zinc in preference to the copper; but when rubbed with ammonia, it turns white, because the ammonia dissolves out the copper. (Berzelius.)

Properties of Alloys of Copper and Zinc, according to Mallet (*Dingl. polyt. J.* 85, 378.)

1 At. Copper is assumed = 31·6, and 1 At. Zinc = 32·3.

At. Cu	At. Zn	Per cent. Cu	Spec. Grav.	Colour.	Fracture.	Tenacity.	Malleability.	Hardness.	Fusibility.
1	0	100	8·667	r.		24·6	8	22	15
10	1	90·72	8·605	r. y.	c. gr.	12·1	6	21	14
9	1	98·80	8·607	r. y.	f. gr.	11·5	4	20	13
8	1	88·60	8·633	r. y.	f. gr.	12·8	2	19	12
7	1	87·30	8·587	r. y.	f. gr.	13·2	0	18	11
6	1	85·40	8·591	y. r.	f. f.	14·1	5	17	10
5	1	83·02	8·415	y. r.	f. f.	13·7	11	16	9
4	1	79·65	8·448	y. r.	f. f.	14·7	7	15	8
3	1	74·58	8·397	pale y.	f. f.	13·1	10	14	7
2	1	66·18	8·299	deep y.	f. f.	12·5	3	23	6
1	1	49·47	8·230	deep y.	c. g.	9·2	12	12	6
1	2	32·85	8·263	dark y.	c. gr.	19·3	1	10	6
8	17	31·52	7·721	silv. w.	c.	2·1	v. br.	5	5
8	18	30·36	7·836	silv. w.	v. c.	2·2	v. br.	6	5
8	19	29·17	7·019	light gr.	c.	0·7	v. br.	7	5
8	20	28·12	7·603	ash-gr.	v.	3·2	br.	3	5
8	21	27·10	8·058	light gr.	c.	0·9	br.	9	5
8	22	26·24	7·882	light gr.	c.	0·8	v. br.	8	5
8	23	25·39	7·443	ash-gr.	f. gr.	5·9	s. d.	1	5
1	3	24·50	7·449	ash-gr.	f. gr.	3·1	v. br.	2	4
1	4	19·65	7·371	ash-gr.	f. gr.	1·9	br.	4	3
1	5	16·36	6·605	dark gr.	f. gr.	1·8	br.	11	2
0	1	0	6·895			15·2		23	1

Under *Colour*, *r.* denotes red, *y.* yellow, *gr.* grey, *silv. w.* silver-white. Under *Fracture*, *c. gr.* denotes coarse-grained, *f. gr.* fine-grained, *f. f.* fine fibred, *c.* conchoidal, *v.* vitreous. The numbers under *Tenacity*, denote the weight in tons required to break a rod whose transverse section measures a square inch. Under *Malleability*, *br.* signifies brittle, *v. br.* very brittle, *s. d.* slightly ductile: the malleability is determined at the temperature of 15·5°. Under *Hardness*, the number 1 denotes the maximum.—The compound $ZnCu^5$ is *Prince's metal* or *Bath-metal;* $ZnCu^4$ is German and Dutch brass; $ZnCu^3$ is rolled brass; $ZnCu^2$ is English brass; ZnCu is German brass; Zn^2Cu is German brass for watch-makers. (Mallet.)

Alloys of Copper and Zinc used in the Arts.

a. Tombac.—Obtained by adding zinc to melted copper. Pale yellowish-red, very ductile. Contains 84·5 per cent. of copper and 15·5 of zinc. (Karsten, *Pogg.* 46, 160; also *J. pr. Chem.* 16, 375.) *Dutch metal* is tombac in leaves $\frac{1}{5000}$ of an inch thick.

	a.	*b.*	*c.*	*d.*
Zn	15·5	15·38	16·0	17·5
Cu	84·5	83·08	82·5	82·5
Sn		1·54	1·5	
	100·0	100·00	100·0	100·0

a. Commercial tombac. (Karsten.)—*b.* Antique bracelet from a tomb at Naumburg.—*c.* Elastic Fibula with tongue, made in the Roman pattern, from a tomb at Königsberg. *d.* Antique chain found at Ronneburg. (Göbel, *Schw.* 60, 407.)—The formula $ZnCu^5$ gives 16·67 per cent. zinc to 83·34 per cent. copper.

Pinchbeck, *Prince's metal*, *Similor*, and *Mannheim Gold* are alloys of similar characters in which the proportion of the two metals is not yet fixed. Older data: For Pinchbeck, 18 pts. copper, 1 brass, and 1 zinc; for Prince's metal, 6 pts. copper, 1 zinc; for Similor, 5 pts. copper, 1 zinc, or 82 pts. copper, 10 zinc, 8 tin; for Mannheim gold, 4 pts. copper, 1 zinc.

b. Brass.—Sometimes obtained by fusing together copper and zinc, sometimes by igniting copper with zinc-oxide and charcoal. The purer the copper, the greater is the quantity of zinc that may be added to it without diminishing its ductility. (Karsten.) Specific gravity from 7·8 to 8·4. Very malleable in the cold; brittle at a red heat.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*
Zn	28·5	27·6	28·15	27·63	29·26	27·45
Cu	71·5	71·0	71·36	71·89	70·29	70·16
Sn		trace		0·85	0·17	0·79
Pb		1·3			0·28	0·20
	100·0	99·9	99·51	100·37	100·00	98·60

	g.	*h.*	*i.*
Zn	29·9	31·80	35·30
Cu	70·1	65·80	61·59
Sn		0·25	0·25
Pb		2·15	2·86
	100·0	100·00	100·00

a is commercial brass of unknown origin. (Karsten.)—*b*. The same. (Regnault.)—*c*. Brass from Neustadt Eberswald. (Kudernatsch, *Pogg.* 37, 575.)—*d*. Brass from Augsberg; *e*. from England; *f*. from Heegermühle. (Lavater. *J. pr. Chem.* 3, 198.)—*g*. Brass from Romilly, very malleable, but too tough for the lathe; *h*. from Stollberg; *i*. of unknown origin. (Chaudet. *Ann. Chim. Phys.* 5, 321; also *Schw.* 21, 350.) The formula Zn^2Cu^4 gives 28·57 per cent. zinc to 71·43 copper.

c. Mosaic Gold.—Prepared by fusing equal weights of copper and zinc in a crucible at the lowest possible degree of heat, stirring constantly, and then adding a further quantity of zinc in small portions, till the colour of the fused mixture, after passing through the various shades of brass-yellow, purple-red, and violet, has become perfectly white. The alloy, after casting in the mould and cooling, exhibits the colour of ducat-gold, and does not tarnish by exposure to the air, even in the neighbourhood of the sea. It contains from 52 to 55 pts. [no more?] zinc to 100 copper. (Hamilton & Parker. *Edinb. J. of Sc.* 1826; also *Schw.* 48, 151; also *Pogg.* 8, 78.)

d. Brass-solder.—2 pts. brass to 1 zinc; or if it is to be more ductile, 6 pts. brass, 5 silver, and 2 zinc.

B. Zinco-cupric Carbonate.—*Aurichalcite.*—Blackens and gives off water when heated. In the inner flame, it covers the charcoal with a coating of zinc-oxide; with borax and carbonate of soda, it yields a button of copper. Hydrochloric acid dissolves it readily and with effervescence. (Böttger, *Pogg.* 48, 495.)

	Aurichalcite.		Böttger.
3ZnO	120	44·28	45·84 to 45·62
2CuO	80	29·52	28·19 ,, 28·36
$2CO^2$	44	16·23	16·06 ,, 16·08
3HO	27	9·97	9·95 ,, 9·93
$\{ZnO; CuO\}2CO^2 + 3Aq$	271	100·00	100·04 ,, 99·99

C. ZINCO-CUPRIC SULPHATE.—Crystallizes from a solution containing an excess of zinc-sulphate, in the form of ferrous sulphate with 7 At. water, and from a solution containing excess of cupric sulphate, in the form of the latter with 5 At. water. (Mitscherlich.)—Blue vitriol dissolves very slowly in a saturated solution of zinc-sulphate; but zinc-sulphate dissolves abundantly in a saturated solution of cupric sulphate; in both cases, the undissolved portion of the added salt is converted into a double salt. (Karsten.)

D. SULPHATE OF CUPRIC OXIDE, ZINC-OXIDE, AND POTASH.—Obtained in the same manner as the sulphate of cupric oxide, magnesia, and ammonia. (p. 463.) Pale blue crystals, having the form of sulphate of magnesia and ammonia. (Bette.)

Crystallized: $(KO,SO^3 + ZnO,SO^3 + 6Aq.) + (KO,SO^3 + CuO,SO^3 + 6Aq.)$

				Bette.
2KO	94·4	21·34		21·60
ZnO	40·0	9·04		8·80
CuO	40·0	9·04		8·50
$4SO^3$	160·0	36·17		35·66
12HO	108·0	24·41		25·44
	442·4	100·00		100·00

COPPER AND CADMIUM.

ALLOY.—Formed by fusing the two metals together.—Light yellowish-white, very brittle, having a fine-grained, scaly structure. Contains 54·29 pts. copper to 45·71 cadmium, which volatilizes completely at the melting point of copper. Even a small quantity of cadmium renders copper brittle. (Stromeyer.)

COPPER AND TIN.

A. ALLOY OF COPPER AND TIN.—The arms of the ancients were sometimes made of *Bronze*, an alloy formed of a large quantity of copper with a little tin.—Obtained by fusing the two metals together, generally in a reverberatory furnace; if the mixture is not stirred, two distinct strata are very apt to form, containing very different proportions of the constituent metals. The combination of the metals in equal parts takes place without evolution of light and heat. (Gehlen.)

Properties of Alloys of Copper and Tin, according to Mallet (*Dingl. polyt. J.* 85, 378).

1 At. Copper = 31·6, and 1 At. Tin = 58·9.

	At. Cu : Sn	Per cent. Cu	Spec. Grav.	Colour.	Fracture.	Tenacity.	Malleability.	Hardness.	Fusibility.
	1 : 0	100	8·607			24·6	1	10	16
a.	10 : 1	84·29	8·561	r. y.	f. gr.	16·1	2	8	15
b.	9 : 1	82·81	8·462	r. y.	f. gr.	15·2	3	5	14
c.	8 : 1	81·10	8·459	y. r.	f. gr.	17·7	4	4	13
d.	7 : 1	78·97	8·728	y. r.	v. c.	13·6	5	3	12
e.	6 : 1	76·29	8·750	pale r.	v.	9·7	brittle	2	11
f.	5 : 1	72·80	8·575	pale r.	c.	4·9	brittle	1	10
g.	4 : 1	68·21	8·400	ash-gr.	c.	0·7	friable	6	9
h.	3 : 1	61·69	8·539	dark gr.	lam. gr.	0·5	friable	7	8

	At. Cu Sn	Per cent. Cu	Spec. Grav.	Colour.	Fracture.	Tenacity.	Malleability.	Hardness.	Fusibility
i.	2 : 1	51·75	8·416	grey w.	v. c.	1·7	brittle	9	7
k.	1 : 1	34·92	8·056	whiter	lam. gr.	1·4	brittle	11	6
l.	1 : 2	21·15	7·387		v. gr.	3·9	brittle	12	5
m.	1 : 3	15·17	7·447	still	v. gr.	3·1	8, tough	13	4
n.	1 : 4	11·82	7·472	whiter	v. lam.	3·1	6, tough	14	3
o.	1 : 5	9·68	7·442		earthy	2·5	7,	15	2
	0 : 1	0	7·291			2·7		16	1

For the abbreviations and the meaning of certain expressions, see the observations following the table on page 479.—*a*, *b*, and *c* are gun-metal; *d* is hard brass for pin-makers; *e* to *i* is bell-metal; *k* and *l*, bell-metal for small bells; *m*, *n*, and *o*, speculum-metal. (Mallet.)

a. Copper alloyed with a very small quantity of tin becomes so hard and brittle when hammered cold, that it requires to be again heated to full redness. (Karsten.)

b. 32 pts. copper to 1 tin: resists the solvent action of hydrochloric acid much more completely than pure copper, and is therefore adapted for the sheathing of ships. (Mushet, *Phil. Mag. J.* 6, 444.)

c. 19 pts. copper to 1 tin: Golden yellow, hard, malleable.

d. From 8 to 11 pts. copper to 1 tin: yellow and slightly malleable: *Gun-metal.* The best proportion appears to be 9 pts. copper to 1 tin.—The alloy of 11 pts. copper to 1 tin appears uniform, after slow cooling, to the unassisted sight; but when examined with a lens, it appears to be composed of striated faces of a reddish alloy mixed with a white one. If it be more quickly solidified by pouring it into thick iron moulds, an alloy is obtained which appears perfectly uniform, even under the lens. When quickly cooled in water after continued strong ignition, it remains uniform; but if suffered to cool slowly after continued ignition, it becomes variable in composition, like that which has been slowly cooled after fusion. Hence the alloy which is uniform at the melting heat, and likewise at a strong red heat, separates into two different alloys when slowly cooled. The large mass of a cannon cannot be cooled, even by moulds which conduct heat well, suddenly enough to prevent the formation of two distinct alloys, whereof the one that is richer in copper solidifies first, while that which is richer in tin, containing 82·3 p. c. copper to 17·7 tin, partly rises to the top, and partly sinks into the mould. (Karsten, *Schw.* 65, 387.)

e. 6·25 pts. copper to 1 tin: the densest of all the alloys; its specific gravity is 8·87. (Briche.)

f. From 4 to 5 pts. copper to 1 tin: *Bell-metal.* Yellowish-grey, and, when very slowly cooled from a red heat, very hard, difficult to file, sonorous, brittle, exhibiting a fine-grained fracture. When heated to redness, and then suddenly cooled by immersion in water, it becomes soft, and easy to file and turn, but may be hardened again by ignition and slow cooling. The Chinese cymbals called *Gong-gongs* are made of this alloy. (Darcet, *Gilb.* 56, 104; further *Ann. Chim. Phys.* 54, 331.) Bell-metal becomes malleable at a temperature not far below redness. (Wollaston, *Gilb.* 56, 106.)—An alloy of 4 pts. copper and 1 tin fused and then very slowly cooled, exhibits a striated surface, a dingy white, close fracture, and is very brittle. When poured out into cold iron moulds, it exhibits the same properties; but if immersed in cold water, after being kept for some time at a low red heat, it becomes yellowish-white and extensible. During the ignition, if somewhat too strong, white globules of an alloy

richer in tin are seen to ooze out, but at a higher temperature, when the whole mass becomes liquid, they disappear. Hence the alloy appears to be resolved at a temperature below its melting point, into two other compounds, which, on slow cooling, reunite and form the brittle alloy, but remain separated if the cooling be more sudden.

g. 3 pts. copper to 1 tin: reddish-white; very brittle; sp. gr. 8·879. (Chaudet.) With a small quantity of arsenic it forms a speculum-metal. (Little.)

h. 2 pts. copper to 1 tin: steel-grey, very hard. Remains uniform, even after slow cooling from a state of fusion. (Karsten.)—2 parts copper, 1 tin, and $\frac{1}{10}$ arsenic form a speculum-metal; so likewise do 64 pts. copper, 33 tin, 2·5 arsenic, and 8 brass. (Little.)

i. 1 pt. copper to 1 tin: bluish-white like zinc, slightly malleable, not very hard; specific gravity 8·468 (Chaudet), 8·79 (Briche). Remains uniform after slow as well as after sudden cooling. (Karsten.)

k. 1 pt. copper to 2 tin: white, brittle. Uniform, even after slow cooling. (Karsten.)

l. 1 pt. copper to 3 tin: bluish-white, exhibits a crystalline aspect and fibrous texture; cracks under the hammer. Specific gravity 7·813. (Chaudet.)

m. 1 pt. copper to 3·6 tin=$CuSn^2$.—In a tinned copper boiler, regular six-sided prisms were found to be formed, with indistinct cleavage parallel to *p.* (Miller, *Phil. Mag. J.* 6, 107.) Yellow-greenish-white; shining; ductile; of specific gravity 7·53; fusing at a red heat; slowly attacked by dilute, easily by strong nitric acid; dissolves rapidly in boiling hydrochloric acid. (Roth, *Pogg.* 36, 478.)

			Roth.
Cu	32	31·33	21·88
Sn^2	118	68·67	77·63
$CuSn^2$	150	100·00	99·51

n. 1 pt. copper to 10 tin: malleable to a certain extent, but cracks under the hammer; specific gravity 7·472. (Chaudet.)

Boiling hydrochloric acid extracts tin from these alloys, and leaves a compound containing a large quantity of copper with a small quantity of tin. (Chaudet, *Ann. Chim. Phys.* 7, 275.)

Ancient and other alloys.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*
Sn	12	22·02	19·66	26·74	26·0	19·5
Cu	88	77·60	80·27	73·00	71·0	80·5
Zn					1·8	
Fe					1·2	
	100	99·62	99·93	99·74	100·0	100·0

a. Bronze from Celtic vessels, swords and spears. (Clarke, *Ann. Phil.* 7, 73.)—*b.* Arrow-head from an Egyptian tomb.—*c.* Cast coffin from Altai, on the borders of China.—*d.* Another coffin. (Göbel, *Schw.* 60, 407.)—*e.* Old bell at Rouen, known by the name of *Cloche d'Argent.* (Gérardin, *Ann. Chim. Phys.* 50, 205.)—*f.* Chinese *Gong.* (Thomson, *Ann. Phil.* 2, 209.)

B. Cuprous Stannate.—The solution of protochloride of tin in caustic potash forms, with cupric nitrate, a yellowish-green precipitate, which, if kept from contact with the air, turns yellow, and is subsequently

C. Cupric Oxide with Lead-oxide.—Produced in the form of a dark-coloured, fused mass in the cupellation of cupriferous silver with lead.

D. Sulphide of Copper and Lead.—*a.* 1 part of galena heated to whiteness in a charcoal crucible with 1 pt. of disulphide of copper, yields a black radiated mass, resembling disulphide of copper.—*b.* One part of galena and 3 parts of disulphide of copper form a compound having a texture similar to that of galena itself. (Fournet.)—*c.* Copper fused even in great excess with galena, does not abstract all the sulphur, but forms an alloy of copper and lead, and a compound of sulphide of copper with sulphide of lead. (Karsten.)

E. *Hyposulphite of Cupric Oxide and Lead-oxide ?*—Hyposulphite of lead-oxide and potash forms with acetate of cupric oxide, a light green precipitate, which turns dark brown on exposure to the air, and, when heated in a retort, is resolved into water, sulphurous acid, and a fused residue, which afterwards solidifies and presents a red surface. The liquid from which the precipitate has separated, contains copper and lead, and turns black when heated. (Rammelsberg, *Pogg.* 56, 314.)

F. Selenide of Copper and Lead.—*a.* 4PbSe,CuSe.—Specific gravity, from 7·4 to 7·5. Reddish lead-grey, yielding a greyish-black powder. Decrepitates strongly when heated in a glass tube, yielding a sublimate of selenium, and fusing to a brownish-yellow liquid, which, after longer heating, solidifies in a black, tumefied mass. When heated on charcoal, it gives off a brown-red fume, with a strong odour of selenium, and fuses to a black slag, covering the charcoal, first with a metallic film, and then with a yellow film of lead-oxide. With borax it forms a pale green glass, and a malleable globule of metal containing lead. With nitric acid it behaves like *b.* (Kersten, *Pogg.* 46, 265.)

					Kersten. From Tannglasbach.
4Pb	416	....	64·20	.....	63·82
Cu	32	....	4·94	.....	4·00
5Se	200	....	30·86	.....	29·35
Ag		....		.....	0·07
Fe and S		....		.....	trace
Quartz		....		.....	2·06
	648	....	100·00	.....	99·30

b. 2PbSe,CuSe.—*Selenide of Copper and Lead, Selenkupferblei* of mineralogists.—From Tilkerode: massive, of specific gravity 7·0, and fine-grained fracture, tending sometimes to the conchoidal, sometimes to the even. Of a lighter lead-grey colour and fainter lustre than selenide of lead; often with a brass yellow or violet tarnish; yields a grey powder. When heated in a glass tube open at both ends, it yields a sublimate of selenium and selenious acid, and fuses to a black slag surrounded with fused yellowish oxide of lead. (Zinken, *Pogg.* 3, 275.) Does not yield a sublimate of selenium when heated in a closed glass tube. (H. Rose, *Pogg.* 3, 290.) From Tannenglasbach. Cleavage-plane apparently parallel to the faces of a cube. Specific gravity from 6·96 to 7·04. Fine-grained, very much like granular galena, but of a darker lead-grey colour; yields a greyish-black powder. When heated in a closed glass tube, it decrepitates slightly—yields a sublimate of selenium (which, after strong and

continued ignition, amounts to 4·7 per cent., that is to say, to half the quantity of selenium combined with the copper)—swells up, and fuses to a translucent mass, which on cooling turns black, but exhibits a yellow colour on the edges, solidifies after long-continued ignition, and exhibits copper-coloured specks on its surface. When heated in an open glass tube, it likewise emits a faint odour of sulphurous acid, and yields a sublimate of selenium, which is afterwards converted into selenious acid. On charcoal it gives off a brown-red fume with a strong odour of selenium—forms a shining, blackish-grey deposit, and afterwards, nearer to the heated substance, a yellow deposit—and leaves a black slag, copper-coloured in parts. In the inner flame, it imparts a beryl-green colour to borax, and yields a grey, malleable button of metal. Dissolves in cold, moderately strong nitric acid, forming a greenish-blue solution, and leaving a residue of selenium. (Kersten.)

	Selenkupferblei.			H. Rose.		Kersten.
2Pb	208	57·78	59·67	to 57·13	.....	53·74
1Cu	32	8·89	7·86	,, 9·55	.....	8·02
3Se	120	33·33	29·96		.....	30·00
Fe		....	0·33		Ag	0·05
Fe and Pb		....	0·44		Fe^2O^3	2·00
Undecomposed ore		....	1·00		S	trace
					Quartz	4·50
	360	100·00	99·26		.....	98·31

c. PbSe,CuSe.—*Selenide of Lead and Copper, Selenbleikupfer* of mineralogists. Found in small fragments. Specific gravity 5·6. Very soft, somewhat malleable. The colour on a recent fracture is between lead-grey and violet, or perfectly violet (the violet pieces give off selenide of mercury when heated—H. Rose). Behaves like *b* before the blowpipe—fuses, however, with still greater facility. (Zinken.) Does not evolve selenium when heated in a closed glass tube. (H. Rose.)

	Selenbleikupfer.			H. Rose. From Tilkerode.
Pb	104	48·15	.....	47·43 to 50·27
Cu	32	14·81	.....	15·45 ,, 14·23
2Se	80	37·04	.....	34·26
Ag		....	.....	1·29
PbO and Fe^2O^3		....	.....	2·08
	216	100·00	.....	100·51

When selenide of lead is fused with diselenide of copper (prepared by strongly igniting copper with selenium), a compound is obtained, which fuses more readily than diselenide of copper; this compound is capable of taking up an additional quantity of selenium, which it does not give off when heated to redness in close vessels. (H. Rose.)

G. Chromate of Cupric Oxide and Lead-oxide.—*Vauquelinite.*—Belongs to the oblique prismatic system. Very small needles and stalactitic masses. Specific gravity from 6·8 to 7·2. Harder than gypsum. Has an adamantine lustre; is translucent, and of a blackish-green colour inclining to olive-green, siskin-green, and yellow; powder siskin-green. On charcoal before the blowpipe it swells up slightly, and then fuses with strong intumescence to a dark grey bead, having the metallic lustre and surrounded with small granules of metal. In carbonate of soda on

b. Antimonial Copper-glance, or *Prismatoidal Copper-glance.*—Crystalline system the right prismatic. *Fig.* 61 with *t*- and *i*-faces; cleavage parallel to *t*. Specific gravity 5·7 (5·782, *Schrötter*). Harder than gypsum. Blackish lead-grey, yielding a powder of the same colour. (Mohs.) Heated in a glass tube, it gives off water, sulphur, and sulphide of arsenic, and leaves a red-brown slag. Heated on charcoal, it effervesces, deposits a yellow and white film, and fuses to a lead-grey metallic bead, which, after continued roasting, yields a button of copper with carbonate of soda. (Schrötter, *Zeitschr. Phys. Math.* 8, 284.)

	Antimonial copper-glance.				Schrötter.		
2Pb	208	....	28·42	.....	29·90	to	26·42
4Cu	128	....	17·49	.....	17·35	,,	16·33
Sb	129	....	17·62	.....	16·65	,,	16·41
As	75	....	10·24	.....	6·04	,,	8·17
12S	192	....	26·23	.....	28·60	,,	28·60
Fe		....		.....	1·40	,,	1·31
HO		....		.....	2·31	,,	2·31
	732	....	100·00	.....	102·25	,,	99·55

$2PbS,4CuS,SbS^3,AsS^3$; or $2PbS,AsS^3 + 4CuS,SbS^3$?

K. Sulphide of Bismuth, Copper, and Lead.—*Needle-ore.*—Six-sided needles, with longitudinal cleavage. Specific gravity 6·12 (Karsten), 6·757 (Frick). Soft and with a mild lustre. Steel-grey, yielding a blackish-grey powder. When heated in an open tube, it yields sulphurous acid and a white deposit, fusing into clear drops and partly volatile, and leaves a metallic granule surrounded with fused black oxide, which becomes transparent and greenish-yellow on cooling. The metallic globule gives a slight copper reaction with fluxes, and yields a granule of copper after long blowing. Needle-ore melts and fumes upon charcoal, covering it with a yellow deposit, and yields a metallic globule having the appearance of bismuth. (Berzelius.) Dissolves in nitric acid with separation of lead-sulphate and a small quantity of sulphur.

	Needle-ore.				Frick.				John.
2Pb	208	....	35·80	.....	35·69	to	36·05	....	24·32
2Cu	64	....	11·02	.....	11·79	,,	10·59	....	12·10
Bi	213	....	36·66	.....	34·62	,,	36·45	....	43·20
6S	96	....	16·52	.....	16·05	,,	16·61	....	11·58
Ni ?		....		.....		,,		....	1·58
Te ?		....		.....		,,		....	1·32
	581	....	100·00	.....	98·15	,,	99·70	....	94·10

The formula corresponds to that of Bournonite (p. 487), excepting that Sb is replaced by Bi.

L. Alloy of Copper, Lead, Tin, and Zinc.—*a British Bell-metal* contains 5·6 per cent. zinc, 10·1 tin, 4·3 lead, and 80·0 copper. (Thomson, *Ann. Phil.* 2, 209.)—*b. Biddery ware* is produced in India by combining 2 pts. tin, 4 lead, and 16 copper, and fusing 3 pts. of the resulting alloy with 16 of zinc. (Wilkins, *Ann. Phil.* 2, 471.)

Copper and Iron.

A. Alloy of Copper and Iron.—Combination between these two metals takes place with difficulty.—100 parts of copper may be made to unite by fusion with any quantity of bar-iron from 1 part to 100 and upwards. The intensity of the copper colour increases till the quantities of the two metals become equal; but the more the quantity of the iron exceeds that of the copper, the paler does the alloy become on the fractured surface. The alloy of 2 pts. copper to 1 iron has the greatest tenacity; if the proportion of iron be increased, the hardness increases but the tenacity diminishes, and the fracture then becomes laminar.—From ores containing the sulphides of iron and copper, the following alloys containing different proportions of the two metals may be prepared. One alloy of this kind was copper-red on the outer surface, had a pale uniform fracture, and was magnetic. Another exhibited externally a copper-red colour inclining to grey; had a deep copper-coloured and laminated fracture; was magnetic, and interspersed with isolated granules of copper and a few granules of iron. A third was iron-coloured, hard; had a laminar fracture; was strongly magnetic; and exhibited isolated granules of copper and numerous granules of iron. (Mushet, *Phil. Mag. J.* 6, 81.)—According to former statements, the alloy of copper and iron is grey, slightly extensible, more difficult to fuse than copper, and magnetic even when it contains only $\frac{1}{10}$ part of iron. The brittleness of iron at a red heat appears sometimes to proceed from admixture of copper.

B. Carbide of Copper and Iron.—Carbon interferes with the combination of iron and copper. (Mushet.) Copper impairs the quality of steel (Faraday & Stodart); and in the proportion of 2 per cent. renders it brittle (Bréant).—*a.* 19 pts. of steel fused with 1 part of copper form an alloy having a radiated crystalline surface, harder than cast-steel, but not available for the ordinary purposes of steel, inasmuch as it will not take an edge; the presence of copper in the alloy is apparent. —*b.* 10 pts. steel with 1 copper. Less crystalline, hard, and brittle; exhibits a few isolated specks of copper.—*c.* 5 pts. steel to 1 copper. Less intimately combined, has a granular fracture, and exhibits a copper colour on the filed surface.—*d.* 3 pts. steel to 1 copper. Part of the copper settles down below the steel, and separate particles of copper are likewise seen on the fractured surface.—White cast-iron behaves with copper in the same manner as steel, but the combination is less intimate, and the quantity of copper taken up does not exceed $\frac{1}{20}$; grey cast-iron takes up still less. (Mushet.)

C. Sulphide of Copper and Iron.—*a. Purple Copper, Variegated Copper, Phillipsine.*—Cubes and cubo-octohedrons, with indistinct cleavage parallel to the octohedral faces. Specific gravity 4·9 to 5·1. Hardness equal to that of calcspar. The colour of the recently fractured surface is between copper-red and pinchbeck-brown, but it quickly acquires a particoloured tarnish; powder greyish-black.—Does not give off sulphur when ignited out of contact of air; when heated in an open glass tube, it yields a large quantity of sulphurous acid, but no sublimate. Heated on charcoal before the blowpipe, it acquires a dark tarnish, then becomes black, and red on cooling. Fuses easily to a brittle globule which becomes magnetic after sufficient blowing, and appears greyish-red

on the fractured surface. When roasted for a considerable time and then treated with a small quantity of borax, it yields a button of copper; and if fused with carbonate of soda after the sulphur has been completely expelled, it yields separate granules of copper and iron. After roasting, it exhibits with fluxes the reactions of cupric and ferric oxide. (Berzelius.) When moistened with hydrochloric acid, it colours the blowpipe-flame blue.

The analyses of Purple Copper lead to no general formula. Either there are different varieties of Purple Copper to be distinguished, or it must be supposed that there is but one kind, probably Fe,3Cu,3S (since the crystallized mineral exhibits this composition), but that this mineral is altered in composition by admixture of variable quantities of disulphide of copper, Copper-pyrites, &c. The analyses correspond to the following calculations:

	At.	I.	*a.*	At.	II.	*b.*
Fe	4	112	17·95	1	28	14·84
Cu	11	352	56·41	3	96	56·76
S	10	160	25·64	3	48	28·24
Quartz			0·12			
		624	100·00		172	100·00
			99·39			99·84

	At.	III.	*c.*	At.	IV.	*d.*
Fe	2	56	14·89	1	28	13·70
Cu	7	224	59·58	4	128	62·75
S	6	96	25·53	3	48	23·55
Quartz			26·98			0·50
		376	100·00		204	100·00
			100·02			99·32

	At.	V.	*e.*	*f.*	*g.*
Fe	1	28	11·11	11·81	11·57	11·53
Cu	5	160	63·50	63·34	63·03	62·70
S	4	64	25·39	24·70	25·06	25·70
Quartz						0·03
		252	100·00	99·85	99·66	99·96

	At.	VI.	*h.*	*i.*	*k.*
Fe	1	28	7·69	7·54	7·9	7·13
Cu	8	256	70·33	69·73	70·0	70·44
S	5	80	21·98	22·65	20·0	22·43
		364	100·00	99·92	97·9	100·00

	At.	VII.	*l.*
Fe	1	28	6·8	6·41
Cu	9	288	69·9	71·00
S	6	96	23·3	22·58
		412	100·0	99·99

a. is massive Purple Copper from Märtanberg in Dalarne. (Plattner, *Pogg.* 47, 351.)—*b.* Crystallized, from the Condurra mine in Cornwall. (Plattner.)—*c.* Cubes from a locality unknown. The difference between this analysis and that of *b*, is perhaps due to admixture of cupric oxide. (Varrentrapp.)—*d.* Purple Copper from Ross Island. (Phillips.)—*e.* From Westmanland. (Hisinger.)—*f.* Massive, from the Woitzki mine on the shores of the White Sea.—*g.* From Bristol in Connecticut. (Bodemann.) —*h.* Massive, from Eisleben. (Plattner.)—*i.* From Nadaud. (Berthier.) —*k.* From Montecastelli. (Berthier.)—*l.* Massive, from Sangershausen. (Plattner.)

From the above calculations I. to VI. two sets of formulæ may be deduced, accordingly as we suppose the Purple Copper to contain FeS, or as Plattner prefers, Fe^2S^3.

Calculation I. gives: $4FeS, CuS + 5Cu^2S$. To make the second formula applicable in this case, Plattner supposes that the ore contains FeS as well as Fe^2S^3.

Calculation II. gives $FeS, CuS + Cu^2S$; or, $Fe^2S^3 + 3Cu^2S$.

Calculation III. $2FeS, CuS + 3Cu^2S$; the second formula is inapplicable.

Calculation IV. $FeS + 2Cu^2S$; the second formula is inapplicable.

Calculation V. $FeS, CuS + 2Cu^2S$, or $Fe^2S^3 + 5Cu^2S$.

Calculation VI. $FeS + 4Cu^2S$, the second formula is inapplicable.

Calculation VII. $FeS, CuS + 4Cu^2S$, or $Fe^2S^3 + 9Cu^2S$.

Since the supposition that the mineral contains FeS, produces the best accordance between the calculated and analytical results, we may fairly give it the preference.

Purple copper heated in a current of hydrogen suffers some loss of weight; viz., *a*, from 2·19 to 2·59 per cent.; *f*, 2·06 to 2·66; *h*, 0·86 to 1·03; and *l*, 1·0 to 1·1 per cent. This loss proceeds partly from sulphur, Fe^2S^3 being converted into FeS [or 2CuS into Cu^2S], partly from oxygen contained in oxide of copper accidentally present, in which case, particles of reduced copper are found after treating the mineral with hydrogen gas. (Plattner.)

b. Copper-pyrites.—Crystalline system the square prismatic. Primary form, *Fig.* 23; $e : e' = 109° 54'$; $e : e'' = 108° 40'$; *Fig.* 24, irregular tetrahedrons produced by obliteration of the four alternate faces of *Fig.* 23. Acute octohedron, *Fig.* 21, $e : e'' = 126° 11'$, and other forms. Specific gravity 4·16. Of the hardness of fluorspar. Does not give sparks with steel. Brass-yellow, often with a variegated tarnish; yields a greenish-black powder.—Before the blowpipe, it behaves like purple copper. (Berzelius.) Dissolves in aqua-regia with separation of sulphur, less readily in nitric acid.—When heated to redness in a charcoal crucible, it gives off 9 per cent. of sulphur. (Berthier.)

100 parts of copper-pyrites ignited with 50 parts of litharge, fuse with intumescence and separation of 6 parts of ductile lead, into a pasty mass which solidifies to a brown glassy slag on cooling.—With 100 parts of litharge, the mass boils up, yields 35 parts of lead, 11·5 of a grey substance, and a glassy slag on the top of all.—With 200 pts. litharge; 49 pts. lead, a small quantity of grey matter upon that, and a translucent, dark brown-red slag as the uppermost stratum.—With 300 pts. litharge: The mass fuses readily, almost without ebullition, yielding 72 parts of lead and a dense, shining, light grey slag. Hence, in the separation of gold from auriferous pyrites, it is necessary to use about three times the weight of litharge, in order to ensure the complete formation of the slag. (Berthier, *Ann. Chim. Phys.* 39, 256.)

			H. Rose.		Phillips.		Hartwall.
Copper-pyrites.			*a.*	*b.*	*c.*	*d.*	*e.*
Fe	28	30·44	30·47	30·00	32·20	30·80	30·03
Cu	32	34·78	34·40	33·12	30·00	31·20	32·20
2S	32	34·78	35·87	36·52	35·16	34·46	36·33
Matrix			0·27	0·39	0·50	1·10	0·93
As, Pb and loss					2·14	2·44	
					Mn^2O^3, and earthy matter		1·30
	92	100·00	101·01	100·03	100·00	100·00	100·79

	Berlin					Quenneville.	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	32·3	33·0
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	30·2	30·5
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	37·0	35·0
[illegible]	[illegible]		[illegible]	[illegible]	[illegible]		
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	99·5	98·5

[illegible] 1. [illegible] from Lundberg in Savoia.—2. Crystallized [illegible] from [illegible]. The crystallized copper-pyrites from [illegible] the same [illegible] [illegible] 1882.—3. Crystallized [illegible]—4. [illegible] copper-pyrites.—5. Copper-pyrites from [illegible]—6. [illegible] from Allegre.—7. from Allevard.—8. [illegible]—9. [illegible]—10. [illegible]—11. From Cornelles.—12. From [illegible]—13. From [illegible]

The [illegible] of copper-pyrites is either $FeS.CuS$ or $Fe_2S_3.CuS$. [illegible] the proportions of the [illegible]

[illegible] SULPHATE.—[illegible] of copper.—[illegible] the names of [illegible], *Liquid*, [illegible] sometimes formed by dissolving [illegible] formed by the weathering of white [illegible] taking up oxygen [illegible] The crystals of this salt [illegible] when [illegible] of the rest of that [illegible] when [illegible] less than 1 per [illegible] These crystals which have the form of [illegible] Their other [illegible] is the [illegible] copper predominates.

[illegible] (*Journ. Chem. Soc.* [illegible])

[illegible] AND [illegible].—[illegible] Grey [illegible] Grey [illegible] explained by the [illegible] of the [illegible] The [illegible] the regular system of [illegible] [illegible] Chemistry [illegible]

[illegible]—[illegible] Fig. 1, 2, 3, 4. [illegible] Steel-grey [illegible] black. [illegible] with a blue flame and [illegible] [illegible] a magnetic [illegible]

	A.			Kobell.	Philips.	Hermann.
Fe		45	[illegible]	[illegible]	[illegible]	14·1
As				trace		
Cu	1·5	33·2	[illegible]	45·[illegible]	45·12	45·4
As	1	13·1	[illegible]	[illegible]	11·54	11·5
S	[illegible]	[illegible]	[illegible]	[illegible]	38·74	31·6
Quartz				[illegible]	3·00	3·0
		[illegible]	100·00	99·45	100·18	100·3

$$FeS + CuS + 4(FeS + 2AsS) = 4[FeS + 2AsS] + 4CuS.AsS.$$

[illegible]enbach found in Tennantite from Cornwall 0·017 per cent. of silver [illegible] 43·8 of copper.

β. *Light Grey Copper.*—(Containing a large quantity of arsenic in addition to antimony.) Specific gravity about 4·5 or 4·7. Steel-grey inclining to lead-grey; yields a black powder.

	At.			H. Rose. a.	At.			H. Rose. b.
Zn	5	160	3·34	3·69	4	128	2·58	2·76
Fe	8	224	4·68	4·66	8	224	4·51	4·89
Ag				0·60	1	108	2·17	2·37
Cu	11 + 48	1888	39·45	40·60	11 + 48	1888	37·99	38·63
Sb	5	645	13·48	12·46	7	903	18·17	16·52
As	7	525	10·97	10·19	5	375	7·54	7·21
S	84	1344	28·08	26·83	84	1344	27·04	26·33
Quartz				0·41				
		4786	100·00	99·44		4970	100·00	98·71

a. From Markirchen in Alsace $=(5ZnS, 8FeS, 11CuS) + 24Cu^2S + (5SbS^3, 7AsS^3) = 4[(\frac{5}{24}Zn, \frac{8}{24}Fe, \frac{11}{24}Cu)S] + (\frac{5}{6}Sb, \frac{1}{6}As)S^3 + 4Cu^2S, AsS^3$.—*b.* From Gersdorf near Freiberg $=(4ZnS, 8FeS, 1AgS, 11CuS) + 24Cu^2S + (7SbS^3, 5AsS^3) = 4[\frac{4}{24}Zn, \frac{8}{24}Fe, \frac{1}{24}Ag, \frac{11}{24}Cu)Sb]S^3 + 4Cu^2S(\frac{1}{6}Sb, \frac{5}{6}As), S^3$.—According to Weissenbach, *b* has a density of 4·722, and contains 1·77 per cent. of silver and 38·5 of copper.

γ. *Dark Grey Copper.*—(Containing little or no arsenic associated with the antimony.) Specific gravity 4·7 to 4·9. Colour iron-black inclining to steel-grey. When rich in zinc, it yields a dark red powder; e. g., *a*, *b*, *c*.

	At.			H. Rose. a.	At.			H. Rose. b.
Zn	6	192	5·64	6·85	10	320	6·90	7·29
Fe	2	56	1·65	1·52	1	28	0·60	0·86
Ag				0·83				0·62
Cu	8 + 32	1280	37·62	38·42	11 + 44	1760	38·05	37·98
Sb	7	903	26·55	25·27	9	1161	24·96	23·94
As	1	75	2·20	2·26	2	150	3·22	2·88
S	56	896	26·34	25·03	77	1232	26·27	25·77
		3402	100·00	100·18		4651	100·00	99·34

	At.			H. Rose. c.
Zn	5	160	6·00	5·55
Fe	2	56	2·10	2·27
Ag	1	108	4·05	4·97
Cu	4 + 24	896	33·61	34·48
Sb	6	774	29·03	28·24
S	42	672	25·21	24·73
		2666	100·00	100·24

a. From the Aurora at Dillenburg; sp. gr. 4·846; contains 0·56 silver and 38·5 copper.

$$(6ZnS, 2FeS, 8CuS) + 16Cu^2S + (7SbS^3, AsS^3) =$$
$$4[\tfrac{6}{16}Zn, \tfrac{2}{16}Fe, \tfrac{8}{16}Cu)S], SbS^3 + 4Cu^2S(\tfrac{3}{4}Sb, \tfrac{1}{4}As)S^3.$$

b. From Kapnik in Hungary; sp. gr. 4·75; contains 1·01 per cent. silver and 37·6 copper. (Weissenbach.)

$$(10ZnS, FeS, 11CuS) + 22Cu^2S + (9SbS^3, 2AsS^3) =$$
$$4[\tfrac{10}{22}Zn, \tfrac{1}{22}Fe, \tfrac{11}{22}Cu)S], SbS^3 + 4Cu^2S, (\tfrac{7}{11}Sb, \tfrac{4}{11}As)S^3.$$

c. From Zilla near Clausthal:

$$(5ZnS, 2FeS, 1AgS, 4CuS) + 12Cu^2S + 6SbS^3 =$$
$$4[\tfrac{5}{11}Zn, \tfrac{2}{11}Fe, \tfrac{1}{11}Ag, \tfrac{4}{11}Cu)S], SbS^3 + 4Cu^2S, SbS^3.$$

	At.			Brunsis. d.	At.			Sandor. e.
Zn	1	32	3·70	5·02				
Fe	1	28	3·25	4·42	2	56	4·10	4·5
Ag				1·09	1	108	7·90	8·9
Cu	2+8	320	37·13	37·11	3+12	480	35·11	35·7
Sb	2	258	29·93	25·97	3	387	28·31	29·8
S	14	224	25·99	23·76	21	336	24·58	24·1
Pb				0·54				0·9
Undecomposed				0·47				
		862	100·00	98·38		1367	100·00	100·9

d. Massive Fahl-ore from Durango in Mexico:

$$(1ZnS,1FeS,2CuS) + 4Cu^2S + 2SbS^3 = 4[(\tfrac{1}{4}Zn,\tfrac{1}{4}Fe,\tfrac{2}{4}Cu)S],SbS^3 + 4Cu^2S,SbS^3.$$

e. Crystallized, from Clausthal:

$$(2ZnS,1FeS,3CuS) + 12Cu^2S + 3SbS^3 = 4[(\tfrac{2}{4}Zn,\tfrac{1}{4}Fe,\tfrac{3}{4}Cu)S],SbS^3 + 4Cu^2S,SbS^3.$$

3. *Silver Fahl-ore.*—(Dark grey copper rich in silver.)—*a.* The *Graugiltigerz* of Wolfach forms dodecahedrons with tetrahedral and cube-faces, and of specific gravity 5·007. (Weissenbach.)—*b.* The so-called *Crystallized Weissgiltigerz* from Freiberg occurs in tetrahedrons and yields a black powder. (H. Rose.)

	At.			H. Rose.	Klaproth.
Zn	3	96	3·24	3·10	
Fe	4	112	3·78	3·72	7·00
Ag	5	540	18·23	17·71	13·25
Cu	24	768	25·93	25·23	25·50
Sb	6	774	26·14	26·63	27·00
S	42	672	22·68	23·52	25·50
		2962	100·00	99·91	98·25

	At.			H. Rose.
Zn	2	64	1·45	0·99
Fe	12	336	7·63	5·98
Ag	2+11	1404	31·88	31·29
Cu	21	672	15·25	14·81
Sb	8	1032	23·43	24·63
S	56	896	20·36	21·17
		4404	100·00	98·87

Graugiltigerz:

$$(3ZnS,4FeS,5AgS) + 12Cu^2S + 6SbS^3 = 4[(\tfrac{3}{12}Zn,\tfrac{4}{12}Fe,\tfrac{5}{12}Ag)S]\,SbS^3 + Cu^2S,SbS^3.$$

Weissgiltigerz:

$$(2ZnS,12FeS,2AgS) + (5\tfrac{1}{2}Ag^2S,10\tfrac{1}{2}Cu^2S) + 12SbS^3 =$$
$$4[(\tfrac{2}{12}Zn,\tfrac{12}{12}Fe,\tfrac{2}{12}Ag)S],SbS^3 + 4[(\tfrac{5\frac{1}{2}}{4}Ag^2,\tfrac{10\frac{1}{2}}{4}Cu^2)S],SbS^3.$$

It is here assumed that the greater part of the silver contained in *Weissgiltigerz* is in the state, not of protosulphide of silver, AgS, but of disulphide, Ag^2S, and replaces part of the copper. (*vid. inf.*)

With respect to another variety of *Weissgiltigerz*, which does not appear to belong to Fahl-ore, *vid.* Weissenbach (*J. techn. Chem.* 10, 215), and with respect to different varieties of *White Copper-ore, vid.* Breithaupt, *Pogg.* 58, 281; 59, 325).

4. *Quicksilver Fahl-ore.*—(Dark grey copper, containing mercury.)—*a.* From Val di Castello. Massive, of specific gravity 5·092, iron-black;

yields a dark red-brown powder. When heated alone in a glass flask, it yields a small quantity of a red-brown sublimate, but with carbonate of soda it gives off mercury. Heated in an open glass tube, it evolves sulphurous acid and antimonic oxide. On charcoal it fuses readily, depositing an areola of zinc-oxide near the assay, and of antimonic oxide at a greater distance. Completely decomposed by aqua-regia and likewise by nitric acid, though less quickly. (Kersten, *Pogg.* 59, 131.)—*b.* From Kutterbach near Iglo. (H. Rose & Scheidthauer, *Pogg.* 58, 161.)

	Kersten.									Scheidt-hauer.
	At.		*a.*		At.		*b.*			
Zn	6	192	5·45	6·05	1	32	0·66			1·01
Fe	3	84	2·39	1·89	8	224	4·63			4·90
Hg	1	100	2·84	2·70	4	400	8·26			7·52
Ag				0·33						trace
Cu	6+32	1216	34·55	35·80	9+44	1696	35·03			35·90
Sb	8	1032	29·32	27·47	8	1032	21·32			18·48
As					3	225	4·65			3·98
S	56	896	25·45	24·17	77	1232	25·45			23·34
Pb										trace
Quartz										2·73
		3520	100·00	98·41		4841	100·00			97·86

$$a. = (6ZnS, 3FeS, 1HgS, 6CuS) + 16Cu^2S + 8SbS^3$$
$$= 4[(\tfrac{6}{16}Zn, \tfrac{3}{16}Fe, \tfrac{1}{16}Hg, \tfrac{6}{16}Cu)S], SbS^3 + 4Cu^2S, SbS^3.$$
$$b. = (1ZnS, 8FeS, 4HgS, 9CuS) + 22Cu^2S + 8SbS^3 + 3AsS^3$$
$$= 4[(\tfrac{1}{22}Zn, \tfrac{8}{22}Fe, \tfrac{4}{22}Hg, \tfrac{9}{22}Cu)S], SbS^3 + 4Cu^2S, (\tfrac{5}{11}Sb, \tfrac{6}{11}As)S^3.$$

In the preceding calculation of the several varieties of Fahl-ore, the following general formula has been assumed as the foundation:

$$4MS, RS^3 + 4M^2S, RS^3.$$

MS denotes the protosulphides of zinc, iron, mercury, silver, and copper; M^2S, disulphide of copper and sometimes also disulphide of silver (a compound not known in the separate state, but analogous to the dioxide of silver and therefore possible). RS^3 is tersulphide of arsenic or antimony. Almost all the calculations correspond very nearly to the analytical results, excepting that the analyses generally show a deficiency of sulphur, arsenic, and antimony,—these substances, in Rose's method of analysis, having been converted, by treating the mineral with chlorine, into volatile chlorine compounds, which it was difficult to condense completely.

H. Rose, to whose admirable investigations we are primarily indebted for the more exact knowledge of the stoïchiometrical composition of Fahl-ore, assigns to it the formula:

$$4MS, RS^3 + 2(4MS^2, RS^3).$$

This formula, however, is not so simple as the preceding; moreover, in the case of Silver Fahl-ore, it requires that the atomic weight of silver be reduced from 108 to 54, and consequently, that the compound hitherto regarded as protosulphide of silver, AgS, be considered as a disulphide, Ag^2S, so that in the second term of the formula, $2(4M^2S, RS^3)$ it may be able to take the place of the deficient Cu^2S. Since, however, silver-oxide is isomorphous with potash and soda (I. 88), this halving must likewise be extended to the atoms of potassium and sodium, a change which would considerably complicate the formulæ of their compounds.

F. Alloy of Copper, Iron, and Zinc.—80 pts. zinc, 1 pt. copper, and 1 pt. cast-iron from Sorel's *White Brass*. This alloy has the aspect and fracture of ordinary zinc; is as hard as copper and tougher than cast-iron; may be turned, filed, and bored; and does not rust even in damp situations. (Berthier. *Pogg.* 52, 344.)

G. Sulphostannate of Iron and Copper.—*Tin-pyrites.*—Specific gravity from 4·35 to 4·454; harder than calcspar; steel-grey inclining to brass-yellow; yields a black powder.—When strongly ignited upon charcoal, it fuses, with evolution of sulphurous acid and formation of white stannic oxide, which covers the assay and the parts of the charcoal nearest to it, and cannot be removed by continuing the blast. After long roasting on the charcoal, it yields a brittle metallic globule, which colours fluxes like iron and copper. When fused, after continued roasting, with a mixture of carbonate of soda and borax, it yields a hard, pale red, somewhat brittle globule of metal. (Berzelius.) Nitric acid dissolves it readily, forming a blue solution and separating stannic oxide and sulphur.

Tin-pyrites from Cornwall:

	At.			Kudernatsch.	Klaproth.	Johnston.
Zn				1·77		10·11
Fe	2	56	13·02	12·44	12·0	4·79
Cu	4	128	29·77	29·39	30·0	23·55
Sn	2	118	27·44	25·55	26·5	31·62
S	8	128	29·77	29·64	30·5	29·93
Matrix				1·02		
		430	100·00	99·81	99·0	100·00

$2FeS.SnS^2 + 2CuS.SnS^2$.—According to Weissenbach, the Cornish Tin-pyrites contains 0·02 per cent. of silver and 28 per cent. of copper; that from Zinnwald, 0·017 p. c. silver and 24·6 p. c. copper.

Copper and Cobalt.

Cobaltoso-cupric Sulphate.—Long, oblique rhombic prisms, like those of green vitriol, and with very nearly the same angles. [Green vitriol, however, contains but 7 atoms of water, and this salt contains 10 atoms.] Dark bottle-green by reflected, but rose-red by transmitted light; has an astringent metallic taste, and is easily soluble in water. (Liebig. *Schar.* 47, 495.)

	Crystallized.		Liebig.
2CoO	75	14·85	14·82
CuO	40	7·92	7·50
$3SO^3$	120	23·76	23·43
30HO	270	53·47	53·01
$2(CuO,SO^3 + 10Aq.) + CoO,SO^3 + 10Aq.$	505	100·00	98·76

According to Mitscherlich, this salt, when it contains an excess of cobalt-sulphate, has the form of green-vitriol and contains 7 atoms of water.

COPPER AND NICKEL.

A. ALLOY OF NICKEL AND COPPER.—Very extensible; colour inclining to white in proportion to the quantity of nickel. According to Geitner, it tarnishes by exposure to the air more quickly than German silver.—A small quantity of copper destroys the magnetic power of nickel, but the smallest addition of iron restores it. (Erdmann, *Schw.* 48, 138.)

10 pts. copper to 1 nickel: pale copper-red, perfectly ductile.—10 pts. copper to 2 nickel: reddish-white.—10 pts. copper to 3 nickel: almost white.—10 pts copper to 4 nickel: perfectly white; on the touchstone, it exhibits the whiteness of silver. (Frick, *Schw.* 48, 141.)

Old slags from disused mines at Suhl contain white granules of metal, which are now extracted and sent into the market as *Suhlian Nickel-silver* (*Suhler Weisskupfer*). According to Brandes (*Schw.* 39, 17), the alloy thus obtained is composed of 8·75 nickel, 88 copper, 0·75 sulphur and antimony, and 1·75 iron, silica and alumina.

B. NICCOLO-CUPRIC SULPHATE.—When the proportion of cupric sulphate is comparatively small, the crystals of this salt have the form of green vitriol and contain 7 atoms of water; with a larger quantity of cupric sulphate, they have the form of the latter, and contain 5 atoms of water. (Mitscherlich.)—The crystals examined by Brewster & Fyfe (*Schw.* 33, 345), contained 39·5 nickel-oxide, 5·3 cupric oxide, 25·5 sulphuric acid, and 29·7 water.—Brooke (*Ann. Phil.* 23, 117) obtained oblique prismatic crystals, having the form of *Fig.* 83, but without the α-faces; $i : u$ or $u' = 100° 15'$; $i : f = 117° 30'$; $u' : u' = 83° 30'$. The aqueous solution of these crystals yielded on evaporation and cooling, first crystals of blue vitriol, and then of the double salt, together with crystals of rhombic nickel-sulphate.

C. SULPHATE OF CUPRIC OXIDE, NICKEL-OXIDE, AND POTASH.—Separates from the mixed solution of cuprico-potassic sulphate, and niccolo-potassic sulphate, in prisms similar to those of the ammonio-magnesian sulphate. They are pale green, permanent in the air, give off water and assume a dingy yellow colour when heated, and dissolve in 4 parts of water but not in alcohol. (Bette, *Ann. Pharm.* 14, 279.)

$$(KO, SO^3 + NiO, SO^3 + 6Aq.) + (KO, SO^3 + CuO, SO^3 + 6Aq.)$$

					Bette.
2KO	94·4	....	21·46	....	19·60
NiO	37·5	....	8·52	....	8·70
CuO	40·0	....	9·09	....	8·75
$4SO^3$	160·0	....	36·38	....	35·82
12HO	108·0	....	24·55	....	26·25
	439·9	....	100·00	....	99·12

D. ALLOY OF COPPER, NICKEL, AND ZINC.—*Nickel-silver*, *German Silver*, *White Copper*, *Packfong* (or properly *Packtong*, *i. e* .white copper, according to Schott), *Weisskupfer*, *Neusilber*, *Argentan*, *Maillechort*.

The copper and nickel are first melted together in a crucible, and the zinc then added in pieces previously heated. Or the three metals, in a state of fine division, are mixed together in a crucible, copper being placed at top and at bottom—the whole covered with charcoal-powder, and fused

in an air furnace with a strong draught, the mixture being stirred all the while, to ensure the complete solution of the difficultly fusible nickel. The longer and the more completely the mixture is fused, the more ductile does it become: part of the zinc burns away. (Gersdorff, *Pogg.* 8, 43.)

Properties of the materials.—*a.* 2 pts. copper, 1 nickel, 1 zinc; serves for spoons and forks.—*b.* 5 pts. copper, 2 nickel, 2 zinc; has the colour of silver alloyed with ¼ pt. copper; serves for knife and fork handles, snuffers, &c.—*c.* 3 pts. copper, 1 nickel, 1 zinc; this proportion gives the best alloy for rolling. The addition of 3 parts of lead to 100 pts. of the mixture *c*, or of 2 pts. lead to 100 parts of the mixture *b*, yields an alloy adapted for cast articles, such as candlesticks, spurs, and bells. The additions of 2·5 pts. of iron or steel to 100 parts of alloy renders it much whiter, but likewise harder and more brittle; the iron must be previously fused with a portion of the copper, under a layer of charcoal-powder in the blast furnace, and then melted together with the zinc and nickel and the rest of the copper. (Gersdorff.)—*d.* 8 pts. copper, 3 nickel, and 5 zinc yield very good nickel-silver. (Frick.) An alloy of 10 pts. copper, 1 nickel, and 5 zinc has still a pale yellow colour; that which contains 10 copper, 1 nickel, and 7 zinc, yellowish-white and less ductile than *d*. (Frick.)—Larger quantities of iron do not enter into combination with the nickel-silver as a whole, but unite with part of the copper, nickel, and carbon, forming an alloy which floats like drops of oil on the surface of the nickel-silver. (Erdmann.)

Nickel-silver has a crystalline structure when solidified from fusion. It must therefore be heated to dull redness and cooled again completely, before it is rolled or hammered: when once the crystalline structure has been destroyed, the alloy may be worked like brass. (Gersdorff.) Chinese nickel-silver may be worked even at a dull red heat, but at a stronger heat, it flies to pieces on the slightest stroke of the hammer. (Fyfe, *Edinb. Phil. J.* 7, 69.)—Nickel-silver is harder than silver, and susceptible of a high polish. Its colour approaches that of silver, but is greyer. A mixture of 1 pt. oil of vitriol and 7 parts water turns it white when boiled with it. (Gersdorff.)—It is not magnetic, or but slightly so when it contains a certain amount of iron. It fuses at a bright red heat, the zinc burning away if the air has access to it. When exposed to the air, it acquires a slight yellow tarnish. When immersed in vinegar it becomes coated with verdigris, only at those parts where the air can likewise act upon it (Frick.) In vinegar it becomes greenish black; in wine, dark brown; in solution of common salt, red-brown; in solution of sal-ammoniac or tartaric acid, black with green spots; and in oxalic acid, black. (Darcet, *J. Pharm.* 23, 223.) In water containing $\frac{1}{300}$ of potash-hydrate, it remains bright. (A. Vogel.)

Analyses of Commercial Nickel-Silver.

	Fyfe.	Smith.	O. Henry.	Darcet.		Louyet.			Elsner.
	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
Zn	25·4	17·8	13·6	31·25	17	17·01	22·15	26·05	25·0
Sn					2				
Fe	2·6		trace		3	trace	trace	trace	3·0
Co		3·4							
Ni	31·6	18·8	19·3	18·75	23	19·13	15·05	10·85	13·0
Cu	40·4	60·0	66·0	50·00	55	63·34	62·40	62·63	57·4
	100·0	100·0	98·9	100·00	100	99·48	99·60	99·53	98·4

a. Chinese Packfong, of specific gravity 8·432.—*b*. English nickel-silver, somewhat yellower than the German.—*c*. Parisian Mailleehort; contains also a trace of arsenic, which remains behind when the alloy is dissolved in nitric acid.—*d* and *e*. From unknown sources.—*f*, *g*, and *h*. English nickel-silver, used in Birmingham for articles that are to be plated.—*i*. From Sheffield, distinguished by extraordinary elasticity, used for the friskets of printing-presses.

American Nickel-silver.—1 pt. iron, 1 cobalt, 2 silver, 2 tin, 4 manganese, 24 nickel, 36 zinc, and 96 copper. (Haggenmacher, *J. pr. Chem.* 4, 388.)

Other Compounds of Copper.

With Mercury, Silver, Gold, Platinum, Palladium, Rhodium, Iridium, and Osmium.

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